ARKIV FÖR FYSIK Band 14 nr 33

Communicated 4 June 1958 by OSCAR KLEIN and IVAR WALLER

Electron distribution and energy bands in crystals of metal borides of the type MB_6

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With 6 figures in the text

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SUMMARY

Hybrids of s, p and d orbitals of the atomic L and M shells have been used in order to describe the distribution of the valence electrons of the boron atoms in metal borides of the type MB_6. Those linear combinations of the hybrid orbitals, which form a basis for the different irreducible representations of the symmetry group O_h, have been found. Using these orbitals, Bloch wave functions have been constructed. In a one-electron approximation the corresponding secular equations have been solved numerically by use of the electronic computer Besk. The results show that the M shell orbitals are very important for the explanation of the high stability of the crystal. The experimentally found conductivities of the crystals of type MB_6 have been explained theoretically on account of conduction bands.

A preliminary communication of the present investigation has been given at the conference for physicists in Uppsala in June 1957 and at the summer school in quantum chemistry at Vålådalen in August 1958.

Introduction

The stable crystal structures of the metal borides of the type MB_6 have been experimentally investigated by Kiessling [1]. The notation M in MB_6 is written for the metal atoms, which are either bivalent (Ca, Sr and Ba) or three-valent (Y, La and some others of the rare earths). The metal atoms form a cubic framework in the crystal. In every cubic cell the boron atoms are grouped in regular octahedrons. The unit cell of the crystal is given in Fig. 1 in section 2.

In an earlier investigation by the present author [2], the MB_6 crystals were theoretically treated in a very simple way by extremely rough valence bond methods. On account of the symmetry of the crystal, atomic *d* orbitals of boron were thought to be of some importance. The author also compared the borides MB_6 to each other for different metal atoms. In this connection there was used a rough method of maximum charge density in the boron-boron bond directions in comparison with other directions. The distance from a boron nucleus to the point of maximum value for the electron charge density in these boron–boron bond directions was determined for different values of the orbital exponents of the *d* orbitals. By comparing these distances to the experimentally determined distances between the boron atoms for different metal atoms in the crystals, it was possible to determine the orbital exponents of the *d* orbitals for the valence electrons of boron in the different metal borides. The result showed that the metal borides, ordered in increasing sequence of the ionization potentials of the metals, also were ordered in increasing sequence with respect to the orbital exponents of the *d* orbitals and also with respect to the stability of the borides in decreasing sequence. Thus, the stabilities of the different borides were explained as caused by ionization of the metal atoms.

The MB_6 crystal has been theoretically investigated also by Longuet-Higgins and de V. Roberts [3] in a more accurate way than there has been done in [2], but the approximations used in [3] are still rather rough. These authors found, that the boron valence electrons together with two electrons of an ionized metal atom in MB_6 form a closed shell structure of $2s$ and $2p$ orbitals in each B_6 octahedron. As is seen in section 8, this result is not quite confirmed by the present investigation.

In the computations of the present work the experimentally determined ionization energy and the distances between the atoms of the crystal have been taken for the case CaB_6, where Ca has been considered to be completely ionized ($\lambda = 1$ in (38)). The corresponding values for the other metal borides of the type MB_6 are very nearly the same. The found results are thus supposed to be rather independent of the special kind of metal atoms occurring in the MB_6 crystal.

In the present paper an approximate one-electron treatment of the crystal, yielding a secular equation, is given in section 1. Bloch orbitals have been used here, constructed by use of non-orthogonal localized orbitals of all the cells. In section 2 projection operators of the point symmetry group O_h for the configuration of the atoms inside every cell are used in order to construct basic cellular orbitals for MB_6. In section 3 there is shown that these orbitals give a natural way of approximately factorizing the secular equation. Section 4 gives an approximate one-electron Hamiltonian operator for the crystal. Section 5 gives formulae for construction of the elements in the split secular equations. In section 6, transformation formulae and numerical values for some of the integrals occurring in the secular equations are given. The approximations used in the methods of the present investigation are discussed in section 7. Section 8 gives the numerical results for the energy bands and the electron distribution. These results are discussed in section 9. The appendix contains a derivation of an approximate expression for the Fock operator expressed in the representation of a set of atomic orbitals for the different boron atoms in the crystal.

Since the present investigation is very similar to [3], it might be valuable to compare the approximations used in the present work by those made in [3]. We can distinguish mainly four different points:

1. In [3] the binding energy integrals have been put proportional to the corresponding overlap integrals. In the present work the one-electron two-centre energy integrals of all the different kinds occurring have been accurately computed, the three-centre integrals have been approximately calculated and the two-electron Coulomb interaction integrals have been compensated by use of effective charges.
2. In [3] the one-centre energy integrals have been put equal to each other for all the $2s$ and $2p$ orbitals. This approximation together with the approximation in point 1 cause no energy expressions to occur in the secular equations of [3], which only contain overlap integrals. In the present work the solutions of the secular equations give the energy bands directly.
3. In [3] the tight-binding approximation has been used. This means taking into account only the 5 nearest B neighbours. In the present work the 24 nearest B neighbours and the 8 nearest M neighbours are taken into account. Thus also some integrals connecting edge-centred cells are included. Numerically, this means a factor of about 3 for the $2s$ and $2p$ overlap elements in the present approximation compared with the corresponding elements in the tight-binding approximation. The more distant neighbours are very essential on account of their large number.
4. In [3] only $2s$ and $2p$ orbitals have been taken into account. In the present work also $3s$, $3p$ and $3d$ orbitals are considered. Though the contribution of these orbitals cannot be calculated with satisfactory accuracy, the numerical results show, that these orbitals are very essential for explaining the properties of the crystal.

The first point above certainly yields the greatest difference between the two compared methods. However, also in the present calculations the approximations mentioned under the first point are those which are most unreliable. Hence, the numerical results cannot be supposed to be quite accurate. In spite of this, the qualitative results found by the present calculations seem to be fairly reliable.

1. A one-electron approximation in the solid state theory

Let us consider the Schrödinger wave equation of an arbitrary crystal without any external influence. In the Born–Oppenheimer approximation, we can separate the electronic wave function from that of the nuclei. Furthermore, we will accept the ordinary approximation of considering the nuclei to have fixed positions in the space, and we neglect the thermal energy and the zero point vibration energy of the crystal. Now, let us assume, for simplicity, that there is an even number, $2N$, of electrons in the crystal, and suppose that the crystal is completely diamagnetic. Thus, in neglecting spin-orbit coupling, the total electronic wave function must be an eigenfunction of both S^2 and S_z with the eigenvalues zero, where S is the total electronic spin operator. Since there are $(2N)!/(N!(N+1)!)$ different independent spin functions of this kind, the total electronic wave function generally is a linear combination of these spin functions, where each of them is multiplied by a space wave function of all the electrons. However, in the above-mentioned approximation, the Hamiltonian operator does not affect the spin wave functions. Thus, if we suppose all the electronic states to be doubly occupied, it is sufficient to consider only the space part of the total electronic wave function. Furthermore, we will neglect the correlation between the different electrons. Thus, we can deal with space orbitals of one-electron type only.

Now, let us divide the crystal into equivalent parallelopiped unit cells. Following [3], we will use the notation "site" for the configuration of atoms in the unit cell in what follows. The site can thus be considered as a molecule, which usually does not exist in a free state, but which is stable when forming part of a crystal lattice. We introduce the "site orbitals",

$$\phi_{\mathbf{n}}(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{n}), \tag{1}$$

which are one-electron wave functions localized to the different sites of the crystal. The position vectors of the centres of the sites have been denoted by **n**. The origin of the coordinate system is put at the centre of one of the sites, which we denote "the central site" ($\mathbf{n} = 0$). The position of the electron in this coordinate system is denoted by **r**. The site orbitals are generally not orthogonal to each other for different **n**, and they need not necessarily be normalized. According to Löwdin [4], it is possible to orthogonalize the site orbitals by use of an expansion of the inverse of the square root of the overlap matrix. The elements of this matrix,

$$\langle \mathbf{n} | \mathbf{n} + \mathbf{m} \rangle = \int \phi_{\mathbf{n}}^{*} \phi_{\mathbf{n}+\mathbf{m}} \, d\tau = \Delta_{\mathbf{m}}, \tag{2}$$

depend upon the relative position vector, **m**, of the participating sites. However, orthogonalisation is unnecessary here, when we want to construct crystal orbitals, $\psi_{\mathbf{k}}$, of the Bloch type, since these functions are automatically orthogonal to each other. The connection between the site orbitals and the crystal orbitals is

$$\psi_{\mathbf{k}} = (V \sum_{\mathbf{m}} e^{i\mathbf{k}\mathbf{m}} \Delta_{\mathbf{m}})^{-\frac{1}{2}} \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} \phi_{\mathbf{n}} \tag{3}$$

or

$$\phi_{\mathbf{n}} = V^{-\frac{1}{2}} \sum_{\mathbf{k}} (\sum_{\mathbf{m}} e^{i\mathbf{k}\mathbf{m}} \Delta_{\mathbf{m}})^{\frac{1}{2}} e^{-i\mathbf{n}\mathbf{k}} \psi_{\mathbf{k}}. \tag{4}$$

Here, the sums over **m** and **n** run over all the sites of the crystal, which we consider as infinite in all directions. The crystal orbitals are normalized over the so called "micro-crystal", which is the domain for which they are periodic. The micro-crystal consists of a three-dimensional infinity of sites, and $V = L_1 L_2 L_3$ is its infinite volume, measured in units of the volume of a single cell. Here, L_ν are the side lengths of the parallelopiped micro-crystal measured in corresponding units. The components of **k** in the space of the reciprocal lattice are $2\pi h_\nu / L_\nu$ ($\nu = 1,2,3$), where h_ν runs over the infinite number of integers of the first zone, i.e. $-L_\nu/2 < h_\nu \leqslant L_\nu/2$. According to the reduced zone scheme [5], we get all the crystal orbitals in this way. In the special case, when the site orbitals (4) are orthogonal to each other, (3) turns into the ordinary Bloch wave functions [6]. Also when overlap is included, the crystal orbitals (3) have the properties of Bloch functions, i.e. they might be written as exp ($i\mathbf{k}\mathbf{r}$) times a function, which is periodic over the sites in the crystal. Thus, we have the well-known result, that the crystal orbitals (3) form a basis for the one-dimensional irreducible representations of the Abelian group of those translations, which transform the infinite crystal into itself [6].

Neglecting configurational interaction, we now construct an anti-symmetric wave function of all the electrons in the crystal as a single Slater determinant of the crystal orbitals combined with spin functions. The Schrödinger wave equation then leads to the ordinary Hartree-Fock equations,

$$F\,\psi_{\mathbf{k}} = \varepsilon_{\mathbf{k}}\,\psi_{\mathbf{k}}, \tag{5}$$

where F is the Fock operator and $\varepsilon_{\mathbf{k}}$ are one-electron energy eigenvalues. In terms of matrix elements in the space spanned by (3), we obtain from (5)

$$\varepsilon_{\mathbf{k}} = \langle \mathbf{k}\,|\,H^1\,|\,\mathbf{k}\rangle + \sum_{\mathbf{k}'} \{\lambda_1 \langle \mathbf{k}\,\mathbf{k}'\,|\,H^{12}\,|\,\mathbf{k}\,\mathbf{k}'\rangle - \lambda_2 \langle \mathbf{k}\,\mathbf{k}'\,|\,H^{12}\,|\,\mathbf{k}'\,\mathbf{k}\rangle\}. \tag{6}$$

Here λ_1 and λ_2 are certain numerical coefficients, which have been introduced, since $\psi_{\mathbf{k}}$ are supposed not to be spin orbitals, but doubly occupied space orbitals. H^1 and H^{12} are the one- and two-electron operators respectively occurring in the total Hamiltonian operator,

$$H = H_0 + \sum_i H^i + \frac{1}{2}\sum_{ij}{}' H^{ij}. \tag{7}$$

Introducing the site orbitals (4), it is readily seen that

$$\langle \mathbf{k}\,|\,H^1\,|\,\mathbf{k}\rangle = \int \psi_{\mathbf{k}}^*\, H^1\, \psi_{\mathbf{k}}\, d\tau = \frac{\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\, H^1_{\mathbf{n}}}{\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\, \Delta_{\mathbf{n}}}. \tag{8}$$

Here we have introduced the notation

$$H^1_{\mathbf{n}} = \langle \mathbf{m}\,|\,H^1\,|\,\mathbf{m}+\mathbf{n}\rangle = \int \phi_{\mathbf{m}}^*\, H^1\, \phi_{\mathbf{m}+\mathbf{n}}\, d\tau \tag{9}$$

for the one-electron energy matrix elements in the space spanned by (4). The corresponding overlap matrix elements, $\Delta_{\mathbf{n}}$, are given by (2). A form quite analogous to (8) can be found for the total expression (6) of $\varepsilon_{\mathbf{k}}$ (see appendix):

$$\varepsilon_{\mathbf{k}} = \frac{\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\, F_{\mathbf{n}}}{\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\, \Delta_{\mathbf{n}}}. \tag{10}$$

Here, $F_{\mathbf{n}}$ are given by (72) and form matrix elements of the Fock operator F (cf. (74)).

In the case, when there are many atoms in a single site, it is sometimes convenient to form every site orbital of the type (4) as a linear combination of given atomic orbitals, $\varphi^{\nu}_{\mathbf{n}}$, of the same site, $\mathbf{n}$. The index ν then refers to a certain atom and a certain atomic orbital localized to this atom. This corresponds closely to the ordinary way of constructing molecular orbitals. Thus,

$$\phi_{\mathbf{n}} = \sum_{\nu} C_{\nu}\, \varphi^{\nu}_{\mathbf{n}}, \tag{11}$$

where C_ν are unknown constant coefficients. In introducing (11) into (10), we obtain the following expression for the energy parameters:

$$\varepsilon_{\mathbf{k}} = \frac{\sum\limits_{\nu'\nu''} C_{\nu'}^{*}\, C_{\nu''}\, F_{\mathbf{k}}^{\nu'\nu''}}{\sum\limits_{\nu'\nu''} C_{\nu'}^{*}\, C_{\nu''}\, \Delta_{\mathbf{k}}^{\nu'\nu''}}. \tag{12}$$

Here we have put

$$F_{\mathbf{k}}^{\nu'\nu''} = \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} \int \varphi_{\mathbf{m}}^{\nu'*}\, F\, \varphi_{\mathbf{m}+\mathbf{n}}^{\nu''}\, d\tau. \tag{13}$$

In (13) there occur atomic orbital integrals containing the Fock energy operator F (cf. (75)). The notations $\Delta_{\mathbf{k}}^{\nu'\nu''}$ in (12) stand for expressions in atomic overlap integrals, which are completely analogous to (13). In the appendix the full expression of (13) is given in matrix elements of the one- and two-electron Hamiltonian operators.

We now suppose that the Fock operator occurring in (5) is replaced by an approximate one-electron Hamiltonian operator h, found by assuming a fixed crystal potential, which we shall discuss in section 4. Thus, as is well-known, the eigenvalue equation (5) is equivalent to the variation problem,

$$\delta \varepsilon_{\mathbf{k}} = 0, \tag{14}$$

where $\varepsilon_{\mathbf{k}}$ are one-electron energy eigenvalues closely corresponding to (12). Here we choose the coefficients, C_ν, as variables. Since the ortho-normalisation condition automatically is taken into account in (12), there is not needed any subsidiary condition to the variation problem (14).

As is seen in the appendix, $F_{\mathbf{k}}^{\nu'\nu''}$ depend upon the coefficients C_ν and are thus of course actually not independent of the variation. However, since it is far from practicable to solve the accurate equations, we postulate that $h_{\mathbf{k}}^{\nu'\nu''}$ are independent of the variation, which corresponds to using a fixed crystal potential. The justification of this approximate attempt depends very markedly on the way of choosing the effective energy operator h (cf. section 4).

On account of this statement, it is now readily verified that (12) and (14) give a linear homogeneous system of equations for the coefficients C_ν. The corresponding secular equation,

$$\mathrm{Det}\,\{h_{\mathbf{k}}^{\nu'\nu''} - \varepsilon_{\mathbf{k}}\, \Delta_{\mathbf{k}}^{\nu'\nu''}\} = 0, \tag{15}$$

has the roots $\varepsilon_{\mathbf{k}}^{\mu}$ $(\mu = 1,2,3, \ldots)$ for which the linear system of equations can be solved. To get the energy bands, the secular equation must be solved for different values of $\mathbf{k}$.

In the case of many atoms inside every cell, the degree of the secular equation is often very large. Then it is advisable to try to factorize this equation. This procedure may be facilitated by use of group theory, if the system of atoms of a single site has any degree of symmetry. In the following section we shall make an investigation of this kind for the case of MB_6.

2. Construction of basic site orbitals for MB_6

We shall now attack the problem of simplifying the secular equation (15) by applying a method given by Wigner [7]. Let us first consider a configuration of atoms, which belongs to the symmetry group $\mathbf{G}$. Let $\mathbf{R}$ be an element of $\mathbf{G}$, and denote by

ϕ^{ji} a set of basic orbitals[1] of the jth irreducible representation. Here j and i can take the values $j=1,2,3, \ldots J$ and $i=1,2,3, \ldots l_j$. The matrix elements of $\mathbf{R}$ in this representation,

$$^jR_{ki} = \int \phi^{jk*}\, \mathbf{R}\, \phi^{ji}\, d\tau,$$

are coefficients in the expansion

$$\mathbf{R}\,\phi^{ji} = \sum_k {}^jR_{ki}\, \phi^{jk}. \tag{16}$$

These elements satisfy the well-known orthogonality relations,

$$\sum_{\mathbf{R}} {}^jR^*_{ik}\, {}^{j'}R_{i'k'} = \frac{G}{l_j}\, \delta_{jj'}\, \delta_{ii'}\, \delta_{kk'}, \tag{17}$$

where G is the number of elements of the group. On account of (16) and (17), it is found that

$$\mathbf{P}^{ji} = \frac{l_j}{G} \sum_{\mathbf{R}} {}^jR^*_{ii}\, \mathbf{R} \tag{18}$$

is a projection operator, which gives the "projection" on ϕ^{ji} of any function χ which can be expanded in the complete function space spanned by $\phi^{j'i'}$ [7].

According to Melvin [8] the projection operator (18) can be factorized in order to be more tractable in practical problems. This simplification has, however, not been used explicitly in the present investigation, since it is preferable to use sums rather than products in the special procedure described below (see Tables 1–5). Factorization has been used only for the "local" operators, which are referred to the different octahedron corners of the central site (see Table 3).

The constant factor l_j/G has no practical importance for the problem of finding those basic functions ϕ^{ji}, which correspond to a certain given arbitrary function. Because of that, we will put this factor equal to unity in the following.

Let us now consider the MB_6 crystal. Since both the cube and the octahedron are transferred into themselves by application of the elements of the octahedral group, O_h, the whole crystal belongs to this group. The total number of elements in O_h is 48. In Fig. 1 the axes of rotation for the different elements of the subgroup O of O_h are given. The notations of the symmetry axes occurring in this figure are the same as those used by Melvin [8].

Now we intend to find a set of basic site orbitals, $\phi^{ji}(\mathbf{r})$, of the central site to which we refer the group operators, $\mathbf{R}$, in terms of *spd* hybrid atomic orbitals, localized to the six boron atoms of this site. In order to do this, we apply the projection operator (18) to a linear combination, ϕ, of *spd* hybrids of the type

$$\chi = C_1\varphi_{2s} + C_2\,\varphi_{2p_x} + C_3\,\varphi_{2p_y} + C_4\,\varphi_{2p_z} + C_5\,\varphi_{3s} + C_6\,\varphi_{3p_x} + C_7\,\varphi_{3p_y} + C_8\,\varphi_{3p_z} + $$
$$+ C_9\,\varphi_{3d_{z^2}} + C_{10}\varphi_{3d_{zx}} + C_{11}\,\varphi_{3d_{zy}} + C_{12}\,\varphi_{3d_{xy}} + C_{13}\,\varphi_{3d_{x^2-y^2}}, \tag{19}$$

where the C's are arbitrary constant coefficients and the φ's are Slater atomic orbitals of the L and M shells, localized to one of the octahedron corners in Fig. 1 (cf. (11)). The linear combination goes over all the six corners $A, B, \ldots F$, thus giving $6 \times 13 = 78$ independent coefficients C. In the following we denominate the expansion (19)

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[1] In Melvin's [8] notations these are called symmetry adapted orbitals.

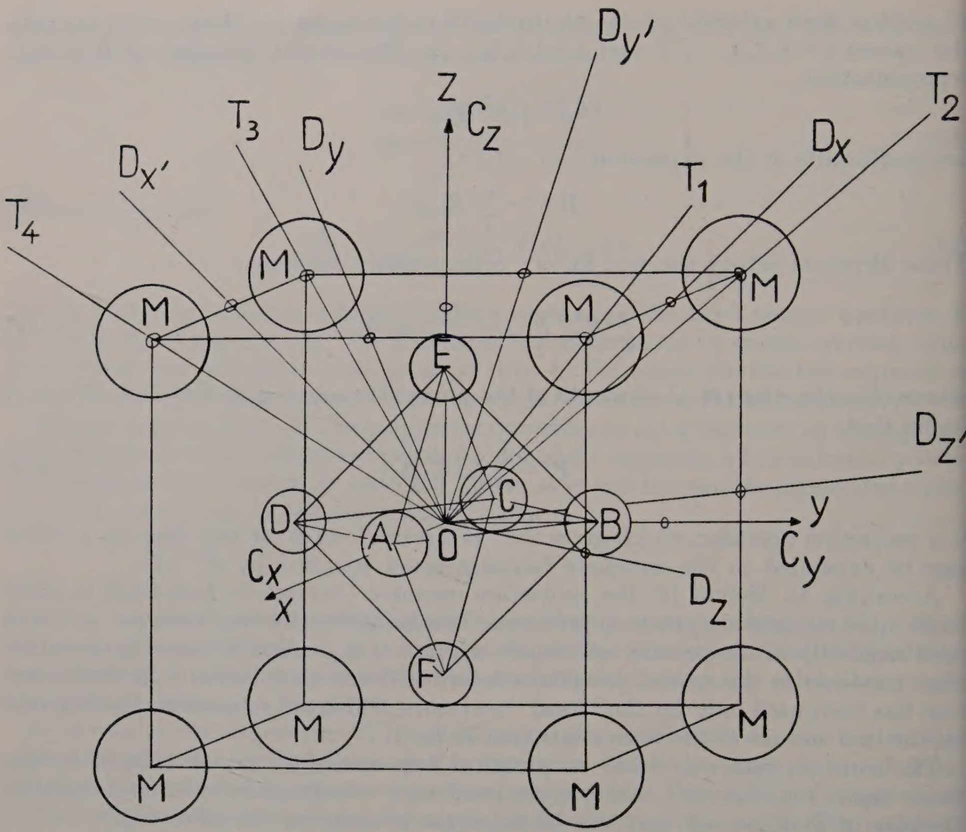

Fig. 1. The unit cell in MB_6. The different boron atoms of the octahedron corners are denoted by A, B, ... F. The metal atoms are denoted by M. Lines denoted by D are two-fold symmetry axes. Lines denoted by T are three-fold symmetry axes. The coordinate lines are four-fold symmetry axes, C_x, C_y and C_z. For the "central site", O is origin also of the crystal coordinate system.

as the *LM* approximation. The corresponding expansion finished by the C_4 term is denoted the *L* approximation.

The different elements of the symmetry group O_h transform (19) into "symmetry orbitals"[1] of the same kind as the original one, but localized to the same or to one of the other corners of the B_6 octahedron. When $\mathbf{R}$ operates on one of the symmetry orbitals the resulting function will be another symmetry orbital. All these symmetry orbitals, which we denote by χ, can be labelled by four suffixes, λ, μ, ν and σ. Here, λ, μ and ν are the Eulerian angles of that rotation, which corresponds to $\mathbf{R}$, divided by $\pi/2$, and σ indicates reflexion. The Eulerian angles are referred to the coordinate system of the central site, given in Fig. 1, where the z-axis has been chosen perpendicular to the line of nodes. Thus, λ can take the values 0, 1 or 2; μ and ν can be 0, 1, 2 or 3. For $\lambda = 0$ and 2, the line of nodes has been chosen in the positive y direction.

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[1] These are usually called "equivalent orbitals" and must not be confused with the symmetry adapted orbitals, ϕ^{ji}.

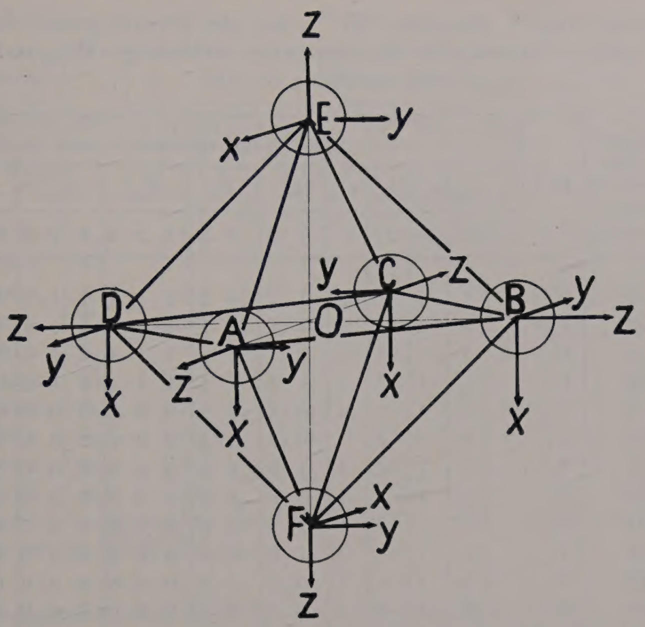

Fig. 2. The local coordinate systems for the different corners A, B, ... F of the B_6 octahedron.

In this case only two suffixes are needed for the Eulerian angles (see the second column in Table 1). The first one of these stands for λ and the second one for $\nu + \mu$, when $\lambda = 0$, and $\nu - \mu$, when $\lambda = 2$. When **R** yields no reflexion, σ is omitted. In other cases σ is replaced by a "local" operator x. A local operator has the property that when it is working on a function localized to the corresponding B atom the result will be a function which is also localized to this B atom. The local operator x means reflexion in a plane perpendicular to the x-axis of the special coordinate system, which belongs to the actual B atom. These different coordinate systems are given in Fig. 2, and have been constructed by the rotation corresponding to λ and μ, of that coordinate system in which the function, $\chi_{00}(x,y,z)$, has been given. The axes of this "original" coordinate system have been chosen parallel to the corresponding axes of the coordinate system of the central site, and its origin is situated at the octahedron corner E on the positive z-axis of the central site coordinate system.

Table 1 gives the coefficients for the symmetry orbitals $\mathbf{R}\chi_{00}$ corresponding to the different group elements **R** in the expansion[1]

$$\phi_{00}^{jl} = \mathbf{P}^{jl}\chi_{00} \tag{20}$$

where $\mathbf{P}^{jl}$ is the projection operator (18) and χ_{00} is the above-mentioned symmetry orbital of type (19). According to (18) these coefficients are the diagonal matrix elements of the different irreducible representations of the inverse group element $\mathbf{R}^{-1}$, since **R** is unitary.

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[1] The complete basic orbital, ϕ^{jl}, is a superposition of orbitals of type (20).

Table 1. Diagonal matrix elements ${}^j(\mathbf{R}^{-1})_{ii}$ for the inverse group elements $\mathbf{R}^{-1}$ of O_h. These are also coefficients for the symmetry orbitals $\chi = \mathbf{R}\,\chi_{00}$ in the expression (20) according to (18).

Group element $\mathbf{R}$ of O_h (1)	Indices for the symmetry orbitals $\chi = \mathbf{R}\,\chi_{00}$	$\mathbf{R}^{-1}$	${}^j(\mathbf{R}^{-1})_{ii}$ for different j's and i's																				
			j	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_g		E_u		T_{1g}			T_{1u}			T_{2g}			T_{2u}		
			i	1	1	1	1	1	2	1	2	1	2	3	1	2	3	1	2	3	1	2	3
$\mathbf{E}$	00	$\mathbf{E}$		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$\mathbf{C}_z$	02	$\mathbf{C}_z$		1	1	1	1	1	1	1	1	–1	–1	1	–1	–1	1	–1	–1	1	–1	–1	1
$\mathbf{C}_x$	22	$\mathbf{C}_x$		1	1	1	1	1	1	1	1	1	–1	–1	1	–1	–1	1	–1	–1	1	–1	–1
$\mathbf{C}_y$	20	$\mathbf{C}_y$		1	1	1	1	1	1	1	1	–1	1	–1	–1	1	–1	–1	1	–1	–1	1	–1
$\mathbf{T}_2$	110	$\mathbf{T}_2^2$		1	1	1	1	0	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_4$	132	$\mathbf{T}_4^2$		1	1	1	1	0	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_2^2$	121	$\mathbf{T}_2$		1	1	1	1	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_4^2$	103	$\mathbf{T}_4$		1	1	1	1	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_1$	101	$\mathbf{T}_1^2$		1	1	1	1	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_3$	123	$\mathbf{T}_3^2$		1	1	1	1	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_1^2$	112	$\mathbf{T}_1$		1	1	1	1	0	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{T}_3^2$	130	$\mathbf{T}_3$		1	1	1	1	0	–1	0	–1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{D}_{z'}$	23	$\mathbf{D}_{z'}$		1	1	–1	–1	0	0	0	0	0	0	–1	0	0	–1	0	0	1	0	0	1
$\mathbf{D}_z$	21	$\mathbf{D}_z$		1	1	–1	–1	0	0	0	0	0	0	–1	0	0	–1	0	0	1	0	0	1
$\mathbf{C}_{4z}^3$	03	$\mathbf{C}_{4z}$		1	1	–1	–1	0	0	0	0	0	0	1	0	0	1	0	0	–1	0	0	–1
$\mathbf{C}_{4z}$	01	$\mathbf{C}_{4z}^3$		1	1	–1	–1	0	0	0	0	0	0	1	0	0	1	0	0	–1	0	0	–1
$\mathbf{C}_{4y}^3$	122	$\mathbf{C}_{4y}$		1	1	–1	–1	1	–1	1	–1	0	1	0	0	1	0	0	–1	0	0	–1	0
$\mathbf{C}_{4y}$	100	$\mathbf{C}_{4y}^3$		1	1	–1	–1	1	–1	1	–1	0	1	0	0	1	0	0	–1	0	0	–1	0
$\mathbf{C}_{4x}^3$	113	$\mathbf{C}_{4x}$		1	1	–1	–1	–1	1	–1	1	1	0	0	1	0	0	–1	0	0	–1	0	0
$\mathbf{C}_{4x}$	131	$\mathbf{C}_{4x}^3$		1	1	–1	–1	–1	1	–1	1	1	0	0	1	0	0	–1	0	0	–1	0	0
$\mathbf{D}_{x'}$	133	$\mathbf{D}_{x'}$		1	1	–1	–1	–1	1	–1	1	–1	0	0	–1	0	0	1	0	0	1	0	0
$\mathbf{D}_x$	111	$\mathbf{D}_x$		1	1	–1	–1	–1	1	–1	1	–1	0	0	–1	0	0	1	0	0	1	0	0
$\mathbf{D}_{y'}$	120	$\mathbf{D}_{y'}$		1	1	–1	–1	1	–1	1	–1	0	–1	0	0	–1	0	0	1	0	0	1	0
$\mathbf{D}_y$	102	$\mathbf{D}_y$		1	1	–1	–1	1	–1	1	–1	0	–1	0	0	–1	0	0	1	0	0	1	0
$\mathbf{i}$	22 x	$\mathbf{i}$		1	–1	1	–1	1	1	–1	–1	1	1	1	–1	–1	–1	1	1	1	–1	–1	–1
$\boldsymbol{\sigma}_{hz}$	20 x	$\boldsymbol{\sigma}_{hz}$		1	–1	1	–1	1	1	–1	–1	–1	–1	1	1	1	–1	–1	–1	1	1	1	–1
$\boldsymbol{\sigma}_{hx}$	00 x	$\boldsymbol{\sigma}_{hx}$		1	–1	1	–1	1	1	–1	–1	1	–1	–1	–1	1	1	1	–1	–1	–1	1	1
$\boldsymbol{\sigma}_{hy}$	02 x	$\boldsymbol{\sigma}_{hy}$		1	–1	1	–1	1	1	–1	–1	–1	1	–1	1	–1	1	–1	1	–1	1	–1	1
$\mathbf{i}\,\mathbf{T}_2$	130 x	$\mathbf{i}\,\mathbf{T}_2^2$		1	–1	1	–1	0	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_4$	112 x	$\mathbf{i}\,\mathbf{T}_4^2$		1	–1	1	–1	0	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_2^2$	103 x	$\mathbf{i}\,\mathbf{T}_2$		1	–1	1	–1	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_4^2$	121 x	$\mathbf{i}\,\mathbf{T}_4$		1	–1	1	–1	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_1$	123 x	$\mathbf{i}\,\mathbf{T}_1^2$		1	–1	1	–1	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_3$	101 x	$\mathbf{i}\,\mathbf{T}_3^2$		1	–1	1	–1	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_1^2$	132 x	$\mathbf{i}\,\mathbf{T}_1$		1	–1	1	–1	0	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$\mathbf{i}\,\mathbf{T}_3^2$	110 x	$\mathbf{i}\,\mathbf{T}_3$		1	–1	1	–1	0	–1	0	1	0	0	0	0	0	0	0	0	0	0	0	0
$\boldsymbol{\sigma}_{vz'}$	03 x	$\boldsymbol{\sigma}_{vz'}$		1	–1	–1	1	0	0	0	0	0	0	–1	0	0	1	0	0	1	0	0	–1
$\boldsymbol{\sigma}_{vz}$	01 x	$\boldsymbol{\sigma}_{vz}$		1	–1	–1	1	0	0	0	0	0	0	–1	0	0	1	1	0	1	0	0	–1

(1) Notations, see e.g. [8] (cf. Fig. 1).

Table 1 (cont.)

Group element $\mathbf{R}$ of O_h (1)	Indices for the symmetry orbitals $\chi = \mathbf{R}\,\chi_{00}$	$\mathbf{R}^{-1}$	${}^{j}(\mathbf{R}^{-1})_{ii}$ for different j's and i's																				
			j	A_{1g}	A_{1u}	A_{2g}	A_{2u}	E_g		E_u		T_{1g}			T_{1u}			T_{2g}			T_{2u}		
			i	1	1	1	1	1	2	1	2	1	2	3	1	2	3	1	2	3	1	2	3
$\mathbf{S}_{4z}^{3}$	23 $\mathbf{x}$	$\mathbf{S}_{4z}$		1	−1	−1	1	0	0	0	0	0	0	1	0	0	−1	0	0	−1	0	0	1
$\mathbf{S}_{4z}$	21 $\mathbf{x}$	$\mathbf{S}_{4z}^{3}$		1	−1	−1	1	0	0	0	0	0	0	1	0	0	−1	0	0	−1	0	0	1
$\mathbf{S}_{4y}^{3}$	102 $\mathbf{x}$	$\mathbf{S}_{4y}$		1	−1	−1	1	1	−1	−1	1	0	1	0	0	−1	0	0	−1	0	0	1	0
$\mathbf{S}_{4y}$	120 $\mathbf{x}$	$\mathbf{S}_{4y}^{3}$		1	−1	−1	1	1	−1	−1	1	0	1	0	0	−1	0	0	−1	0	0	1	0
$\mathbf{S}_{4x}^{3}$	131 $\mathbf{x}$	$\mathbf{S}_{4x}$		1	−1	−1	1	−1	1	1	−1	1	0	0	−1	0	0	−1	0	0	1	0	0
$\mathbf{S}_{4x}$	113 $\mathbf{x}$	$\mathbf{S}_{4x}^{3}$		1	−1	−1	1	−1	1	1	−1	1	0	0	−1	0	0	−1	0	0	1	0	0
$\boldsymbol{\sigma}_{vx'}$	111 $\mathbf{x}$	$\boldsymbol{\sigma}_{vx'}$		1	−1	−1	1	−1	1	1	−1	−1	0	0	1	0	0	1	0	0	−1	0	0
$\boldsymbol{\sigma}_{vx}$	133 $\mathbf{x}$	$\boldsymbol{\sigma}_{vx}$		1	−1	−1	1	−1	1	1	−1	−1	0	0	1	0	0	1	0	0	−1	0	0
$\boldsymbol{\sigma}_{vy'}$	100 $\mathbf{x}$	$\boldsymbol{\sigma}_{vy'}$		1	−1	−1	1	1	−1	−1	1	0	−1	0	0	1	0	0	1	0	0	−1	0
$\boldsymbol{\sigma}_{vy}$	122 $\mathbf{x}$	$\boldsymbol{\sigma}_{vy}$		1	−1	−1	1	1	−1	−1	1	0	−1	0	0	1	0	0	1	0	0	−1	0

(1) Notations, see e.g. [8] (cf. Fig. 1).

Let us now denote by $\mathbf{z}$ a local operator, which means rotation of $\pi/2$ about the "local" z-axis, i.e. the z-axis belonging to the actual one of the corners $A, B, \dots F$ of the B_6 octahedron given in Fig. 2. Let us further introduce the local operators,

$$\left.\begin{aligned} &\boldsymbol{\sigma}_+ = 1 + \mathbf{x}, \qquad \boldsymbol{\sigma}_- = 1 - \mathbf{x}, \\ &\mathbf{0}_\alpha = \sum_\beta C_{\alpha\beta}\,\mathbf{z}^\beta \quad (\alpha = 1, 2, \dots 6;\ \beta = 0, 1, 2, 3). \end{aligned}\right\} \tag{21}$$

Here, as before, $\mathbf{x}$ means reflexion in the yz plane belonging to the actual corner, and the coefficients $C_{\alpha\beta}$ are given in Table 2.

Table 2. The coefficients $C_{\alpha\beta}$ of (21).

α	β: 0	1	2	3
1	1	1	1	1
2	1	−1	1	−1
3	1	0	1	0
4	0	1	0	1
5	1	0	−1	0
6	0	1	0	−1

As we see from Table 1 and the equations (18)–(20) the site functions ϕ_{00}^{ji} are found as sums over atomic orbitals, localized to the different octahedron corners. In carrying out the summations, it is seen that all these corner localized functions can also be found by application of one of the operators $\pm\mathbf{0}_\alpha\boldsymbol{\sigma}_+$, $\pm\mathbf{0}_\alpha\boldsymbol{\sigma}_-$ or zero to the functions χ_{00}, χ_{20} and $\chi_{1\mu 0}(\mu = 0, 1, 2, 3)$ respectively. In Table 3 these operators and the corresponding operands χ are given for the different basic orbitals represented by the

Table 3. Local operators for certain local orbitals found from the starting function χ_{00}. The projection of χ_{00} on a basic orbital, ϕ^{ji}, is found as the sum over all the transformed local orbitals for different corners A, B, ... F.

Irreducible representation j	Row suffix i	Local operators for certain orbitals χ of the resp. corners $A, B, \ldots F$					
		χ_{100}	χ_{110}	χ_{120}	χ_{130}	χ_{00}	χ_{20}
		A	B	C	D	E	F
A_{1g}		$\mathbf{O}_1 (1+\mathbf{x})$	$\mathbf{O}_1 (1+\mathbf{x})$	$\mathbf{O}_1 (1+\mathbf{x})$	$\mathbf{O}_1 (1+\mathbf{x})$	$\mathbf{O}_1 (1+\mathbf{x})$	$\mathbf{O}_1 (1+\mathbf{x})$
A_{1u}		$\mathbf{O}_1 (1-\mathbf{x})$	$\mathbf{O}_1 (1-\mathbf{x})$	$\mathbf{O}_1 (1-\mathbf{x})$	$\mathbf{O}_1 (1-\mathbf{x})$	$\mathbf{O}_1 (1-\mathbf{x})$	$\mathbf{O}_1 (1-\mathbf{x})$
A_{2g}		$-\mathbf{O}_2 (1+\mathbf{x})$	$\mathbf{O}_2 (1+\mathbf{x})$	$-\mathbf{O}_2 (1+\mathbf{x})$	$\mathbf{O}_2 (1+\mathbf{x})$	$\mathbf{O}_2 (1+\mathbf{x})$	$\mathbf{O}_2 (1+\mathbf{x})$
A_{2u}		$-\mathbf{O}_2 (1-\mathbf{x})$	$\mathbf{O}_2 (1-\mathbf{x})$	$-\mathbf{O}_2 (1-\mathbf{x})$	$\mathbf{O}_2 (1-\mathbf{x})$	$\mathbf{O}_2 (1-\mathbf{x})$	$\mathbf{O}_2 (1-\mathbf{x})$
E_g	1	$\mathbf{O}_2 (1+\mathbf{x})$	$-\mathbf{O}_4 (1+\mathbf{x})$	$\mathbf{O}_2 (1+\mathbf{x})$	$-\mathbf{O}_4 (1+\mathbf{x})$	$\mathbf{O}_3 (1+\mathbf{x})$	$\mathbf{O}_3 (1+\mathbf{x})$
E_g	2	$-\mathbf{O}_3 (1+\mathbf{x})$	$-\mathbf{O}_2 (1+\mathbf{x})$	$-\mathbf{O}_3 (1+\mathbf{x})$	$-\mathbf{O}_2 (1+\mathbf{x})$	$\mathbf{O}_3 (1+\mathbf{x})$	$\mathbf{O}_3 (1+\mathbf{x})$
E_u	1	$\mathbf{O}_2 (1-\mathbf{x})$	$-\mathbf{O}_4 (1-\mathbf{x})$	$\mathbf{O}_2 (1-\mathbf{x})$	$-\mathbf{O}_4 (1-\mathbf{x})$	$\mathbf{O}_3 (1-\mathbf{x})$	$\mathbf{O}_3 (1-\mathbf{x})$
E_u	2	$-\mathbf{O}_3 (1-\mathbf{x})$	$-\mathbf{O}_2 (1-\mathbf{x})$	$-\mathbf{O}_3 (1-\mathbf{x})$	$-\mathbf{O}_2 (1-\mathbf{x})$	$\mathbf{O}_3 (1-\mathbf{x})$	$\mathbf{O}_3 (1-\mathbf{x})$
T_{1g}	1	0	$-\mathbf{O}_6 (1+\mathbf{x})$	0	$\mathbf{O}_6 (1+\mathbf{x})$	$\mathbf{O}_5 (1+\mathbf{x})$	$-\mathbf{O}_5 (1+\mathbf{x})$
T_{1g}	2	$\mathbf{O}_5 (1-\mathbf{x})$	0	$-\mathbf{O}_5 (1-\mathbf{x})$	0	$-\mathbf{O}_5 (1-\mathbf{x})$	$\mathbf{O}_5 (1-\mathbf{x})$
T_{1g}	3	0	0	0	0	$\mathbf{O}_1 (1-\mathbf{x})$	$-\mathbf{O}_1 (1-\mathbf{x})$
T_{1u}	1	0	$-\mathbf{O}_6 (1-\mathbf{x})$	0	$\mathbf{O}_6 (1-\mathbf{x})$	$\mathbf{O}_5 (1-\mathbf{x})$	$-\mathbf{O}_5 (1-\mathbf{x})$
T_{1u}	2	$\mathbf{O}_5 (1+\mathbf{x})$	0	$-\mathbf{O}_5 (1+\mathbf{x})$	0	$\mathbf{O}_5 (1+\mathbf{x})$	$\mathbf{O}_5 (1+\mathbf{x})$
T_{1u}	3	0	0	0	0	$\mathbf{O}_1 (1+\mathbf{x})$	$-\mathbf{O}_1 (1+\mathbf{x})$
T_{2g}	1	0	$\mathbf{O}_6 (1+\mathbf{x})$	0	$-\mathbf{O}_6 (1+\mathbf{x})$	$\mathbf{O}_5 (1+\mathbf{x})$	$-\mathbf{O}_5 (1+\mathbf{x})$
T_{2g}	2	$-\mathbf{O}_5 (1-\mathbf{x})$	0	$\mathbf{O}_5 (1-\mathbf{x})$	0	$\mathbf{O}_5 (1-\mathbf{x})$	$\mathbf{O}_5 (1-\mathbf{x})$
T_{2g}	3	0	0	0	0	$\mathbf{O}_2 (1-\mathbf{x})$	$-\mathbf{O}_2 (1-\mathbf{x})$
T_{2u}	1	0	$\mathbf{O}_6 (1-\mathbf{x})$	0	$-\mathbf{O}_6 (1-\mathbf{x})$	$\mathbf{O}_5 (1-\mathbf{x})$	$-\mathbf{O}_5 (1-\mathbf{x})$
T_{2u}	2	$-\mathbf{O}_5 (1+\mathbf{x})$	0	$\mathbf{O}_5 (1+\mathbf{x})$	0	$\mathbf{O}_5 (1+\mathbf{x})$	$\mathbf{O}_5 (1+\mathbf{x})$
T_{2u}	3	0	0	0	0	$\mathbf{O}_2 (1+\mathbf{x})$	$-\mathbf{O}_2 (1+\mathbf{x})$

irreducible representation and a row suffix i. Table 4 shows the effect of working with the different operators occurring in (21) on various functions $F(x,y,z)$, which give the angular parts of the L and M shell orbitals. The result will be unchanged, if F is multiplied by a spherically symmetrical function, $S(r)$, where r is the local radius vector starting from the actual octahedron corner. Introducing for the orbitals χ in the head of Table 3 the linear combination (19) of s, p and d atomic orbitals (which have the same symmetry types as the operands in Table 4), we now easily find the projection of χ_{00} on the basic site orbitals. Repeating the procedure, given by Tables 1–3, for the symmetry orbitals localized to all the other corners of the B_6 octahedron, we finally get the complete basic site orbitals of *spd* type, which are given in Table 5. We have previously denoted these functions by ϕ^{ji}, but here they are characterized by the ordinary notation of the corresponding irreducible representation, with the difference that capital letters have been replaced by lower case letters.

Table 4. The effect of operating with the local operators (21) on certain functions, F.

Operator $\mathbf{O}$	Function $\mathbf{O}\,F$								
$\mathbf{1}$	1	x	y	z	z^2	zx	zy	xy	x^2-y^2
$\mathbf{x}$	1	$-x$	y	z	z^2	$-zx$	zy	$-xy$	x^2-y^2
$\mathbf{1}+\mathbf{x}$	2	0	$2y$	$2z$	$2z^2$	0	$2zy$	0	$2(x^2-y^2)$
$\mathbf{1}-\mathbf{x}$	0	$2x$	0	0	0	$2zx$	0	$2xy$	0
$\mathbf{z}$	1	y	$-x$	z	z^2	zy	$-zx$	$-xy$	$-(x^2-y^2)$
$\mathbf{z}^2$	1	$-x$	$-y$	z	z^2	$-zx$	$-zy$	xy	x^2-y^2
$\mathbf{O}_3=\mathbf{1}+\mathbf{z}^2$	2	0	0	$2z$	$2z^2$	0	0	$2xy$	$2(x^2-y^2)$
$\mathbf{O}_5=\mathbf{1}-\mathbf{z}^2$	0	$2x$	$2y$	0	0	$2zx$	$2zy$	0	0
$\mathbf{O}_4=\mathbf{z}\,\mathbf{O}_3$	2	0	0	$2z$	$2z^2$	0	0	$-2xy$	$-2(x^2-y^2)$
$\mathbf{O}_6=\mathbf{z}\,\mathbf{O}_5$	0	$2y$	$-2x$	0	0	$2zy$	$-2zx$	0	0
$\mathbf{O}_1=\mathbf{O}_3+\mathbf{O}_4$	4	0	0	$4z$	$4z^2$	0	0	0	0
$\mathbf{O}_2=\mathbf{O}_3-\mathbf{O}_4$	0	0	0	0	0	0	0	$4xy$	$4(x^2-y^2)$
$\mathbf{O}_1\,(\mathbf{1}+\mathbf{x})$	8	0	0	$8z$	$8z^2$	0	0	0	0
$\mathbf{O}_1\,(\mathbf{1}-\mathbf{x})$	0	0	0	0	0	0	0	0	0
$\mathbf{O}_2\,(\mathbf{1}+\mathbf{x})$	0	0	0	0	0	0	0	0	$8(x^2-y^2)$
$\mathbf{O}_2\,(\mathbf{1}-\mathbf{x})$	0	0	0	0	0	0	0	$8xy$	0
$\mathbf{O}_3\,(\mathbf{1}+\mathbf{x})$	4	0	0	$4z$	$4z^2$	0	0	0	$4(x^2-y^2)$
$\mathbf{O}_3\,(\mathbf{1}-\mathbf{x})$	0	0	0	0	0	0	0	$4xy$	0
$\mathbf{O}_4\,(\mathbf{1}+\mathbf{x})$	4	0	0	$4z$	$4z^2$	0	0	0	$-4(x^2-y^2)$
$\mathbf{O}_4\,(\mathbf{1}-\mathbf{x})$	0	0	0	0	0	0	0	$-4xy$	0
$\mathbf{O}_5\,(\mathbf{1}+\mathbf{x})$	0	0	$4y$	0	0	0	$4zy$	0	0
$\mathbf{O}_5\,(\mathbf{1}-\mathbf{x})$	0	$4x$	0	0	0	$4zx$	0	0	0
$\mathbf{O}_6\,(\mathbf{1}+\mathbf{x})$	0	0	$-4x$	0	0	0	$-4zx$	0	0
$\mathbf{O}_6\,(\mathbf{1}-\mathbf{x})$	0	$4y$	0	0	0	$4zy$	0	0	0

Furthermore, the index $i=1,2,\ldots l_j$ does not enter in this notation, since for different i's the orbitals differ only by a space rotation. Thus, they have the space degeneracy l_j. Notations such as e.g. $(2s, 2p_z)$, which occur in Table 5, signify linear combinations with arbitrary coefficients of the atomic orbitals inside the brackets. However, the coefficients of equivalent atomic orbitals localized to different octahedron corners $A, B, \ldots F$ are common. The degrees of those parts of the approximately factorized secular equation (see section 3), which correspond to the basic site orbitals ϕ^{ji} in the L and LM approximations resp. are given to the right in Table 5. We note that the projections on a_{1u} of all the orbitals of type (19) are identically zero. Specially, in the L approximation also the projections of χ on the spaces of types a_{2g}, a_{2u} and e_u are identically zero. The symmetries of the non-vanishing basic orbitals in the LM approximation are given by Fig. 3. In the L approximation this result is the same as that of Longuet-Higgins and de V. Roberts [3]. The orbitals may differ only by a similarity transformation.

In the next section, we shall examine an approximate way of factorizing the secular equation by use of the basic orbitals.

Table 5. Transformed local orbitals derived from a linear combination of symmetry orbitals as the starting function.

The complete basic orbitals ϕ^{ji} of *spd* type for the central site are found as sums over all the corners A, B, ... F. The dimensions of the approximately factorized secular equations are also given for the L and LM approximations, resp.

Basic orbital ϕ^{ji}	i	Transformed local orbitals for the resp. corners (1)						Dimension of the secular equ.	
		A	B	C	D	E	F	L	LM
a_{1g}		S	S	S	S	S	S	2	5
a_{1u}		0	0	0	0	0	0	0	0
a_{2g}		$-X$	X	$-X$	X	X	X	0	1
a_{2u}		$-Y$	Y	$-Y$	Y	Y	Y	0	1
e_g	1	$2X$	$X-S$	$2X$	$X-S$	$X+S$	$X+S$	2	6
	2	$-(X+S)$	$-2X$	$-(X+S)$	$-2X$	$X+S$	$X+S$	2	6
e_u	1	$2Y$	Y	$2Y$	Y	Y	Y	0	1
	2	$-Y$	$-2Y$	$-Y$	$-2Y$	Y	Y	0	1
t_{1g}	1	0	x	0	$-x$	y	$-y$	1	3
	2	x	0	$-x$	0	x	x	1	3
	3	y	y	y	y	0	0	1	3
t_{1u}	1	S	$-y$	$-S$	y	x	$-x$	3	8
	2	y	S	$-y$	$-S$	y	y	3	8
	3	x	x	x	x	S	$-S$	3	8
t_{2g}	1	Y	$-x$	$-Y$	x	y	$-y$	1	4
	2	$-x$	Y	x	$-Y$	x	x	1	4
	3	y	$-y$	y	$-y$	Y	$-Y$	1	4
t_{2u}	1	$-X$	y	X	$-y$	x	$-x$	1	4
	2	$-y$	X	y	$-X$	y	y	1	4
	3	x	$-x$	x	$-x$	X	$-X$	1	4
Dimension of the total secular equation								24	78

(1) Notations: $S = (2s, 2p_z, 3s, 3p_z, 3d_{z^2})$; $X = (3d_{x^2-y^2})$; $Y = (3d_{xy})$; $x = (2p_x, 3p_x, 3d_{zx})$; $y = (2p_y, 3p_y, 3d_{zy})$. The coefficients C_μ of (19) occurring in these hybridizations are equal for equivalent local atomic orbitals of a certain basic orbital. The hybrids x and y in the table are equivalent.

3. An approximate factorization of the secular equation

The basic site orbitals, ϕ^{ji}, which have been found for the central site in the preceding section, are automatically orthogonal to each other. Since the group operators commute with the Hamiltonian operator of the system, the energy integrals connecting different basic orbitals of the same site vanish identically. However, the secular equation (15) involves integrals of orbitals localized to different sites. In the LM approximation the degree of this secular equation for every point $\mathbf{k}$ in the wave vector space is 78, in the L approximation this degree is 24 (cf. Table 5). Thus, in order to facilitate the solution of the secular equation, we shall show that matrix elements belonging to different basic orbitals vanish, at least approximately, also in the case when two different sites are involved.

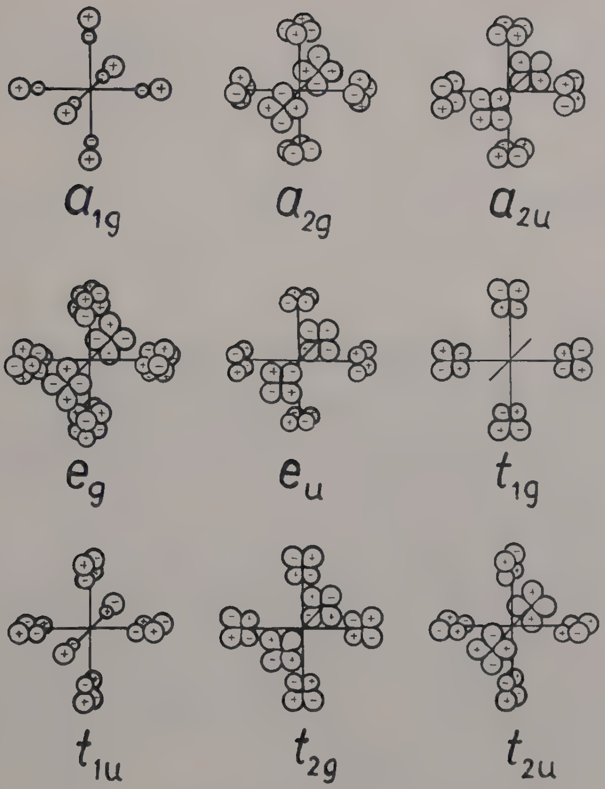

Fig. 3. Symmetry shapes of the basic site orbitals.

In order to do this, we consider the group operator, $\mathbf{R}$, of O_h, which is referred to the central site (see Fig. 1). We denote by $\mathbf{R}_\mathbf{n}$ the corresponding operator referred to the site $\mathbf{n}$. This will be found by a translative movement of the axis of rotation (or the plane of reflexion or the point of inversion) of $\mathbf{R}$ through the distance $\mathbf{n}$. Let us now apply this translation to an arbitrary function, $\phi(\mathbf{r})$, localized to the central site. Then we get the corresponding function, $\phi_\mathbf{n}(\mathbf{r})$, localized to the site $\mathbf{n}$, in accordance with (1). In the case of MB_6, it is now readily seen that

$$\mathbf{R}\phi_\mathbf{n} = \mathbf{R}_\mathbf{m}\phi_\mathbf{m}, \tag{22}$$

where $\mathbf{m} = \mathbf{R}\,\mathbf{n}$ is the position vector of the site, found by the operation of $\mathbf{R}$ on $\mathbf{n}$. In words, (22) means that when a group element belonging to the central site operates on a function $\phi_\mathbf{n}$ localized to the site $\mathbf{n}$ the resulting function is also found by operating on the "translated" function $\phi_\mathbf{m}$ with the corresponding group element localized to this site.

Since $\mathbf{R}$ is a unitary operator commuting with the effective Hamiltonian operator, h, we also have the connection

$$\mathbf{R}^\dagger h \mathbf{R} = h. \tag{23}$$

The basic orbitals, $\phi_{\mathbf{n}}^{jl}$, of the different sites, $\mathbf{n}$, are given by Table 5 and (1). Let us now use these orbitals to construct crystal orbitals, $\psi_{\mathbf{k}}^{jl}$, according to (3). We can then form the matrix elements

$$\int \psi_{\mathbf{k}}^{jl*}\, h\, \psi_{\mathbf{k}'}^{j'l'}\, d\tau \sim \sum_{\mathbf{n}'\mathbf{n}} e^{i(\mathbf{k}'\mathbf{n}'-\mathbf{k}\mathbf{n})} \int \phi_{\mathbf{n}}^{jl*}\, h\, \phi_{\mathbf{n}'}^{j'l'}\, d\tau. \tag{24}$$

The integrals on the right-hand side of (24) contain the positions of the sites only as the difference, $\mathbf{m} = \mathbf{n}' - \mathbf{n}$. By using this property and the relation

$$\sum_{\mathbf{n}} e^{i(\mathbf{k}'-\mathbf{k})\mathbf{n}} = V \cdot \delta_{\mathbf{k}\mathbf{k}'}, \tag{25}$$

it is easily found that

$$\int \psi_{\mathbf{k}}^{jl*}\, h\, \psi_{\mathbf{k}'}^{j'l'}\, d\tau = \delta_{\mathbf{k}\mathbf{k}'} \int \psi_{\mathbf{k}}^{jl*}\, h\, \psi_{\mathbf{k}}^{j'l'}\, d\tau. \tag{26}$$

Thus, the secular equation is factorized for different values of $\mathbf{k}$. For equal basic orbitals ϕ^{jl}, i.e. $j = j'$ and $l = l'$, (26) is also an immediate consequence of (3), since the corresponding Bloch orbitals form a basis for the irreducible representations of the group of unit translations. We have also already anticipated this result in the derivation of the secular equation (15).

The elements of (26), diagonal in $\mathbf{k}$, are given by a relation quite analogous to (10). Let us consider the energy integrals occurring in the numerator of this relation,

$$h_{\mathbf{n}} = \int \phi^{jl*}\, h\, \phi_{\mathbf{n}}^{j'l'}\, d\tau. \tag{27}$$ [1]

Here, for the sake of simplicity, the four basic indices are omitted in the term on the left side. Let us introduce the symmetrical and anti-symmetrical parts of $h_{\mathbf{n}}$:

$$\left.\begin{aligned} S_{\mathbf{n}} &= \tfrac{1}{2}\,(h_{\mathbf{n}} + h_{-\mathbf{n}}); \\ A_{\mathbf{n}} &= \tfrac{1}{2}\,(h_{\mathbf{n}} - h_{-\mathbf{n}}). \end{aligned}\right\} \tag{28}$$

By use of (28) the numerator in the relation analogous to (10) can be written:

$$\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\, h_{\mathbf{n}} = \sum_{\mathbf{n}} \{S_{\mathbf{n}} \cos(\mathbf{k}\,\mathbf{n}) + i\, A_{\mathbf{n}} \sin(\mathbf{k}\,\mathbf{n})\}. \tag{29}$$

Now, we want to examine whether (29) is real or purely imaginary. As we shall soon see, no other case occurs.

In order to make this investigation, let us consider the inversion, $\mathbf{R} = \mathbf{i}$, in O_h. The elements of the irreducible representations for this special group element are

$${}^{j}(\mathbf{i})_{kl} = (-1)^p\, \delta_{kl}. \tag{30}$$

Here, p is the parity of the corresponding basic orbital. The g orbitals of Table 5 and Fig. 3 have $p = +1$ and the u orbitals have $p = -1$. According to (16) and (30) we now find the symmetry properties

$$\mathbf{i}\phi^{jl} = (-1)^p \phi^{jl} \tag{31}$$

which of course are valid also if the inversion operator and the basic orbitals are referred to an arbitrary site, $\mathbf{n}$. Thus, using (22), we have

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[1] When the site index, $\mathbf{n}$, is omitted, ϕ^{jl} is referred to the central site (cf. (1)).

$$\mathbf{i}\,\phi_{-\mathbf{n}}^{j'l'} = \mathbf{i}_{\mathbf{n}}\,\phi_{\mathbf{n}}^{j'l'} = (-1)^{p'}\,\phi_{\mathbf{n}}^{j'l'}, \tag{32}$$

since $\mathbf{i}(-\mathbf{n}) = \mathbf{n}$. On account of the unitarity property, $\mathbf{i}^{\dagger} = \mathbf{i}^{-1} = \mathbf{i}$, and by use of (23), (31) and (32), we now have

$$\begin{aligned}\int \phi^{jl*}\,h\,\phi_{-\mathbf{n}}^{j'l'}\,d\tau &= \int (\mathbf{i}\,\phi^{jl})^{*}\,h\,\mathbf{i}\,\phi_{-\mathbf{n}}^{j'l'}\,d\tau \\ &= (-1)^{p+p'}\int \phi^{jl*}\,h\,\phi_{\mathbf{n}}^{j'l'}\,d\tau.\end{aligned} \tag{33}$$

Using (27) and (33), (28) can be written

$$S_{\mathbf{n}} = \tfrac{1}{2}\,[1 + (-1)^{p+p'}]\,h_{\mathbf{n}}; \qquad A_{\mathbf{n}} = \tfrac{1}{2}\,[1 - (-1)^{p+p'}]\,h_{\mathbf{n}}. \tag{34}$$

As is seen from (34), $S_{\mathbf{n}}$ vanishes, if the participating basic orbitals have different parities. In the case of equal parities, $A_{\mathbf{n}}$ vanishes. Since we have used only real basic orbitals (cf. the preceding section), $h_{\mathbf{n}}$ is always real. Thus, (29) is either real or purely imaginary. This property simplifies the secular equation (15) considerably, since it might be very troublesome to solve this equation, when the elements of the secular determinant are arbitrary complex numbers. We now signify such an element as a "secular element". Let us consider three different cases:

(i) The secular element contains orbitals, belonging to equal basic site orbitals. In this case, the parity is the same for both the orbitals, and $A_{\mathbf{n}}$ vanishes.

(ii) The secular element contains different basic orbitals, and $p \neq p'$. In this case, $S_{\mathbf{n}}$ vanishes, and the secular element is purely imaginary.

(iii). The secular element contains different basic orbitals, but $p = p'$. In this case. $A_{\mathbf{n}}$ vanishes, but $S_{\mathbf{n}} = h_{\mathbf{n}}$ does not generally vanish, except for the central site. Here, the secular element is real.

In order to look further into the cases (ii) and (iii), we will rearrange the terms of the sum on the left side of (29) by use of operation on the sites $\mathbf{n}$ with an arbitrary element $\mathbf{R}^{-1}$ of the group O_h referred to the central site, according to:

$$\begin{aligned}\sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}\,h_{\mathbf{n}} &= \sum_{\mathbf{n}} e^{i\mathbf{k}(\mathbf{R}^{-1}\mathbf{n})}\int \phi^{jl*}\,h\,\phi_{\mathbf{R}^{-1}\mathbf{n}}^{j'l'}\,d\tau \\ &= \frac{1}{G}\sum_{\mathbf{R}}\sum_{\mathbf{n}} e^{i\mathbf{k}(\mathbf{R}^{-1}\mathbf{n})}\sum_{k}\sum_{k'} {}^{j}R_{kl}^{*}\,{}^{j'}R_{k'l'}\int \phi^{jk*}\,h\,\phi_{\mathbf{n}}^{j'k'}\,d\tau.\end{aligned} \tag{35}$$

Here the summation over $\mathbf{R}$ together with division by G plays the rôle of a unity operator, and use has been made of (23), (22) and (16). Now, if $\exp[i\mathbf{k}(\mathbf{R}^{-1}\mathbf{n})]$ always were independent of $\mathbf{R}$, it would appear from (17) that (35) contains the Kronecker symbols $\delta_{jj'}$ and $\delta_{ll'}$ as factors. For the first term in the sum over the sites ($\mathbf{n} = 0$), it is obviously true that this exponential function really is independent of $\mathbf{R}$. That the Kronecker symbols occur as factors in this case is also a direct consequence of ϕ^{ji} forming a basis for the irreducible representations of the symmetry group O_h, referred to the central site. However, for the other terms it does not hold for every $\mathbf{k}$. But, it is certainly fulfilled for all the sites, $\mathbf{n}$, at the following special points in the wave vector space[1]:

$$\mathbf{k} = 0; \qquad \mathbf{k} = \pi(\pm 1, \pm 1, \pm 1), \tag{36}$$

---

[1] For these $\mathbf{k}$ vectors, $\exp[\mathrm{i}\,\mathbf{k}\,(\mathbf{R}\,\mathbf{n})] = \pm 1$, independently of $\mathbf{R}$, i.e. the point group O_h leaves this exponential function invariant.

i.e. for the end points of the energy bands in the corner centred directions. As a matter of fact, when a group operator of O_h is applied to $\mathbf{n}$, one gets the position vector of another site with the same magnitudes of its components. These are only permuted between themselves. Thus, on account of the periodic properties of the exponential function occurring in (35), this exponential function is independent of $\mathbf{R}$ at the end points of the energy bands in the corner centred directions of the $\mathbf{k}$ space. As is seen, this also means that the crystal orbitals $\psi_{\mathbf{k}}$ are symmetry adapted orbitals of O_h at these points, which is a well-known property. On the contrary, there is no other direction in the wave vector space for which the secular equation (15) is properly factorized by use of the basic orbitals, $\phi_{\mathbf{n}}^{jl}$. Thus, for the other directions in the $\mathbf{k}$ space the point group representations will be mixed, but probably not too much. In the vicinity of the points (36) the secular equation is properly factorized, yielding one simplified secular equation for every basic site orbital. Thus, there is rather good reason to believe that even the widths of the bands are only little disturbed by the secular elements in the cases (ii) and (iii). A further reason for believing this is that many of these elements are in fact still zero, and that all the non-vanishing secular elements in these cases are generally much smaller than in the case (i) for arbitrary values of $\mathbf{k}$, at least in the L approximation for MB_6. Thus, we might neglect the secular elements in the cases (ii) and (iii). As a matter of fact, there are many other inevitable approximations in the present investigation, which seem to be much more dubious than this one. This approximation gives an immediate way of factorizing the secular equation (15) for every value of $\mathbf{k}$. We will then get one secular equation for every hybrid basic site orbital given in Table 5. The problem of solving these equations is essentially simplified on account of the fact, that all the secular elements in these equations are real.

The approximate factorization of (15) can be made mainly on account of the relation (22), which is valid for MB_6, since the cubic cell belongs to the same symmetry group, O_h, as the B_6 octahedron. This is not true for crystals in general.

4. The effective one-electron Hamiltonian operator for MB_6

The experimentally determined distances in the crystals of type MB_6 [1] are rather little dependent on the different metal atoms, M, which occur. This is consistent with the fact that an M atom has a considerable space available in one of the "holes" between the B_6 octahedra. Hence the stability of the MB_6 crystal probably depends mainly on the boron framework, and, approximately the M atoms might be considered only as point charges. Furthermore, we shall suppose that the bivalent M atoms are doubly ionized. For the numerical treatment the case M = Ca has been chosen. Thus, the total Hamiltonian operator of the system under consideration can be written

$$H = \sum_i \left(-\tfrac{1}{2}\Delta_i\right) - \sum_i \frac{Z_{B_0}}{r_{iB_0}} + \tfrac{1}{2}\sum_{B_0}\sum_{B\neq B_0} Z_B \left(\frac{Z_{B_0}}{r_{B_0B}} - \sum_i^{(B_0)} \frac{1}{r_{iB}}\right) + \\ + \sum_{B_0}\sum_{M} Z_M \left(\frac{Z_{B_0}}{r_{B_0M}} - \sum_i^{(B_0)} \frac{1}{r_{iM}}\right) + E_I + \tfrac{1}{2}\sum_{M'}\sum_{M''\neq M'} \frac{Z_{M'}Z_{M''}}{r_{M'M''}} + \tfrac{1}{2}\sum_i\sum_{j\neq i}\frac{1}{r_{ij}}. \qquad (37)$$

Here, atomic units have been used. The suffixes B and M refer to the respective kinds of nuclei, and the suffixes i and j to the valence electrons of the boron framework. The notation (B_0) above a summation sign signifies that the sum runs over all the valence electrons at the boron atom B_0. Certainly, the physical idea of referring electrons to certain atoms in the crystal cannot really be applied to molecular or crystal problems in general. But, for this special case it might be done mathematically only as a formal trick in order to divide up the total energy per electron, which is possible, since all the B atoms in the crystal are completely equivalent to each other (cf. (46)).

$Z_B = 3$ is the nuclear charge of each B nucleus unified with its two 1*s* electrons. Introducing λ as the formal degree of ionization, the formal charge of the M ion will be $Z_M = 2\lambda$, where $0 \leqslant \lambda \leqslant 1$. Complete ionization thus corresponds to $\lambda = 1$. For the borides with three-valent M atoms, however, complete ionization would correspond to $\lambda = 1.5$. The mean value of the number of valence electrons at every B atom is equal to $n_B = 3 + \lambda/3$. The term E_I stands for the ionization energy of all the M atoms in the crystal. The constant potential energy of the nuclear charge points has also been added, in order to get the total energy of a lattice with fixed nuclei.

The one-electron operator would correspond to the energy of one electron in the average field of the rest of the crystal. To obtain the total energy (37) as a sum over formal one-electron energies we shall also add a constant term including nuclear energy, but calculated per electron. This term is equal to the energy of one B nucleus unified with its two 1*s* electrons in interaction with the whole system except its own valence electrons, divided by its number of valence electrons, n_B. We note, that it is not meaningless to divide up this energy, on account of the equivalency of all the B atoms in the crystal. The constant ionization energy, $I(\lambda)$, for the degree λ of ionization of one M atom, is computed for Ca by use of experimental data [9]. This has also been portioned out per valence electron of boron and added to the one-electron operator. The resulting operator is:

$$h = -\tfrac{1}{2}\Delta - \sum_{B}^{(24)} \frac{Z_B^{\text{eff}}}{r_B} - \sum_{M}^{(8)} \frac{2\lambda}{r_M} + \frac{1}{1+\lambda/9}\left\{\sum_{B \neq B_0}^{(24)} \frac{Z_B^{\text{eff}}}{r_{BB_0}} + \sum_{M}^{(8)} \frac{2}{r_{MB_0}}\right\} + \frac{1}{18+2\lambda}(I + \lambda^2 \varepsilon_R). \tag{38}$$

Effective Z values occur also in the added constant terms of (38), since these give the interaction between a B nucleus and the other B nuclei together with their electron clouds. The sums over B and M have been performed for the 24 nearest B neighbours and the 8 nearest M neighbours. With increasing order of neighbours the effective charges tend indefinitely towards $-\lambda/3$ (cf. Table 6 of section 5).

The ionic integrals connecting neighbours of the largest distance taken into account have almost the same values as the corresponding terms calculated by using point charges. For the 2*s* orbitals these values are identical in eight figures. This is a reasonable argument for breaking off the sums here (at least for the L shell orbitals). Then, in (38) the remaining energy has been summed up as an electrostatic energy of point charges. In this term, ε_R is the potential energy of one $B_6{}^{2}$ octahedron in the field of those positive and negative ions far apart, which have not been included in the above-mentioned sums. At very large distances the resulting charge of every B ion has for simplicity been considered as placed at the corresponding octahedron centre. Then the contribution to ε_R from concentric cubic shells have been computed separately. Certainly, this expansion might be calculated to give any value depending on the order of summation, since both the positive and negative terms of the expansion yield infinite non-convergent series. However, the total value of this electrostatic energy calculated per electron is very small. As a matter of fact the value calculated by use of the Madelung constant gives about -0.03 a.u. per electron. The corresponding value found by the present method is about -0.09 a.u. Probably the latter is a more realistic value, since the octahedron point charges ought to be split up in six different point charges, giving an increase of the magnitude of the electrostatic energy per electron in the last term, since the electrostatic interaction within the site is not counted here. A comparison with the energy bands of the bonding site orbitals given in the tables and figures of section 8, shows that the constant contribution of this electrostatic energy does not change the bonding properties considerably. The ionization energy, I, has also the same order of magnitude.

All the constant terms, added to the one-electron operator[1], have certainly no influence on the electron distribution, computed by use of the variation principle (14). The energy differences between the various states are also independent of these terms. However, these additional terms will give some information about the stability of the total crystal.

In qualitatively comparing the eigenvalues, ε, of (38) with those of the total operator (37) portioned out "per electron", $\bar{\varepsilon}$, we see that $\varepsilon \approx \bar{\varepsilon}$. Since $\bar{\varepsilon} < 0$ would correspond to a stable state at the absolute temperature zero, we may conclude that the crystal is stable if $\varepsilon < 0$, that is, if the eigenvalues of (38) in the ground state are negative. In a qualitative treatment the mean value of $-\varepsilon$ taken over all the electrons in the ground state might thus be taken as a rough measure of the stability of the crystal.

On account of this approximate way of choosing the zero level of the energy, only the difference between two eigenvalues of (38) may be given a more direct physical interpretation. However, the results of the present investigation show that the zero level of the energy is chosen remarkably well, since all the electrons really occupy bonding orbitals, i.e. orbitals corresponding to negative energy eigenvalues, while most of the unoccupied orbitals are antibonding (see Fig. 6 in section 8).

5. Construction of the secular elements

The basic site orbitals, $\phi_{\mathbf{n}}^{ji}$, found in Table 5, are analogous to (11), and the corresponding secular equations of the type (15) can be solved separately according to section 3. As is seen in Table 5, every $\varphi_{\mathbf{n}}^{ji\nu}$ in the expansion which corresponds to (11) is expressed in terms of atomic orbitals, $\varphi_{\mathbf{n}\mathrm{B}}^{ji\nu}$, localized to the different B atoms of the site $\mathbf{n}$. If we omit the orbital indices j, i and ν, we can write

$$\varphi_{\mathbf{n}} = \sum_{\mathrm{B}}^{(\mathbf{n})} \varphi_{\mathbf{n}\mathrm{B}}, \tag{39}$$

where the sum is taken over those B atoms which belong to the site $\mathbf{n}$. The energy integrals occurring in (10) can then be written (with $F = h$):

$$h_{\mathbf{n}} = \sum_{\mathrm{B}'}^{(\mathbf{m})} \sum_{\mathrm{B}''}^{(\mathbf{m}+\mathbf{n})} \langle \mathrm{B}' | h | \mathrm{B}'' \rangle. \tag{40}$$

Here $\langle \mathrm{B}' | h | \mathrm{B}'' \rangle$ is the energy integral containing the orbitals $\varphi_{\mathbf{m},\mathrm{B}'}^{ji\nu'}$, and $\varphi_{\mathbf{m}+\mathbf{n},\mathrm{B}''}^{ji\nu''}$. The orbital indices are omitted also here. Consequently, for convenience, we can drop the indices ν' and ν'' in the secular energy elements corresponding to (13). Thus, we have

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[1] In the actual computations all the added terms are not exactly constant, since the corresponding effective charges have been given a certain small amount of orbital dependence (see the next section).

$$h_{\mathbf{k}} = \sum_{\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} h_{\mathbf{n}} = \sum_{\mathbf{n}} \cos (\mathbf{k}\,\mathbf{n})\, h_{\mathbf{n}}, \tag{41}$$

since $h_{\mathbf{k}}$ is real according to case (i) of section 3.

Now, let $\boldsymbol{\sigma} = \boldsymbol{\sigma}^{-1}$ be a reflexion operator, yielding reflexion in one of the coordinate planes of the central site. Then, according to (22) and (23)

$$h_{\boldsymbol{\sigma}\mathbf{n}} = \langle 0 | h | \boldsymbol{\sigma}\,\mathbf{n} \rangle = \langle 0 | \boldsymbol{\sigma}\, h\, \boldsymbol{\sigma} | \boldsymbol{\sigma}\,\mathbf{n} \rangle = \langle 0 | \boldsymbol{\sigma}\, h\, \boldsymbol{\sigma}_{\mathbf{n}} | \mathbf{n} \rangle = h_{\mathbf{n}} \tag{42}$$

when both the participating orbitals belong to the same basic orbital. The last step follows, since the non-diagonal matrix elements of $\boldsymbol{\sigma}$ vanish, and thus $\boldsymbol{\sigma}\phi = \pm\phi$ according to (16) and Table 1. The same thing is valid for the inversion and for the operators $\mathbf{C}_x$, $\mathbf{C}_y$ and $\mathbf{C}_z$ of O_h, which signify half round rotation about the respective axis. All these operators have the basic site orbitals as eigenfunctions with the only eigenvalues ± 1 (cf. Table 1). Furthermore, the basic orbitals given in Table 5 always have such a symmetry that at least two coordinate axes are equivalent. Taking these as the y and z directions and using (42), we can write the expansion (41)

$$\begin{aligned} h_{\mathbf{k}} = h_{(0,0,0)} &+ 2 \cos k_x\, h_{(1,0,0)} + 2(\cos k_y + \cos k_z)\, h_{(0,1,0)} + \\ &+ 2\,[\cos (k_x + k_y) + \cos (k_x - k_y) + \cos (k_x + k_z) + \cos (k_x - k_z)]\, h_{(1,1,0)} + \\ &+ 2\,[\cos (k_y + k_z) + \cos (k_y - k_z)]\, h_{(0,1,1)} + \dots, \end{aligned} \tag{43}$$

where the components of $\mathbf{n}$ are explicitly written. Terms connecting sites at larger distances than those occurring in (43) have been neglected in the secular equations. However, $h_{(0,0,0)}$ includes some contribution also from more distant sites. The secular overlap elements, $\Delta_{\mathbf{k}}$ (orbital indices omitted), are completely analogous to (43). For orbitals of the M shell the terms consisting of overlap integrals of the highest order of site neighbours taken into account are very considerable, as is seen in Fig. 4.

Introducing (38) into (43) via (40) we get a lot of integrals of different kinds. Let us, for brevity, introduce certain special notations for some of these integrals:

One-centre integrals: *Two-centre integrals:*

$$\left.\begin{array}{ll} & A_b = \langle \mathrm{B}_0 | \mathrm{B} \rangle; \\ A_0 = \langle \mathrm{B}_0 | \mathrm{B}_0 \rangle; & B_b = \langle \mathrm{B}_0 | 1/r_{\mathrm{B}_0} + 1/r_{\mathrm{B}} | \mathrm{B} \rangle; \\ B_0 = \langle \mathrm{B}_0 | 1/r_{\mathrm{B}_0} | \mathrm{B}_0 \rangle; & C_b = \langle \mathrm{B}_0 | -\tfrac{1}{2}\Delta | \mathrm{B} \rangle; \\ C_0 = \langle \mathrm{B}_0 | -\tfrac{1}{2}\Delta | \mathrm{B}_0 \rangle. & D_b = \langle \mathrm{B}_0 | 1/r_{\mathrm{B}} | \mathrm{B}_0 \rangle; \\ & D_m = \langle \mathrm{B}_0 | 1/r_{\mathrm{M}} | \mathrm{B}_0 \rangle. \end{array}\right\} \tag{44}$$

The index b (or m) for the two-centre integrals stands for the relative position vector between the centres of the two participating atoms. The Mulliken [10] approximation has been used for the three-centre integrals:

$$\left\langle \mathrm{B}' \left| \frac{1}{r_{\mathrm{B}}} \right| \mathrm{B}'' \right\rangle \approx \frac{1}{2} \left(\frac{1}{r_{\mathrm{BB}'}} + \frac{1}{r_{\mathrm{BB}''}} \right) \langle \mathrm{B}' | \mathrm{B}'' \rangle. \tag{45}$$

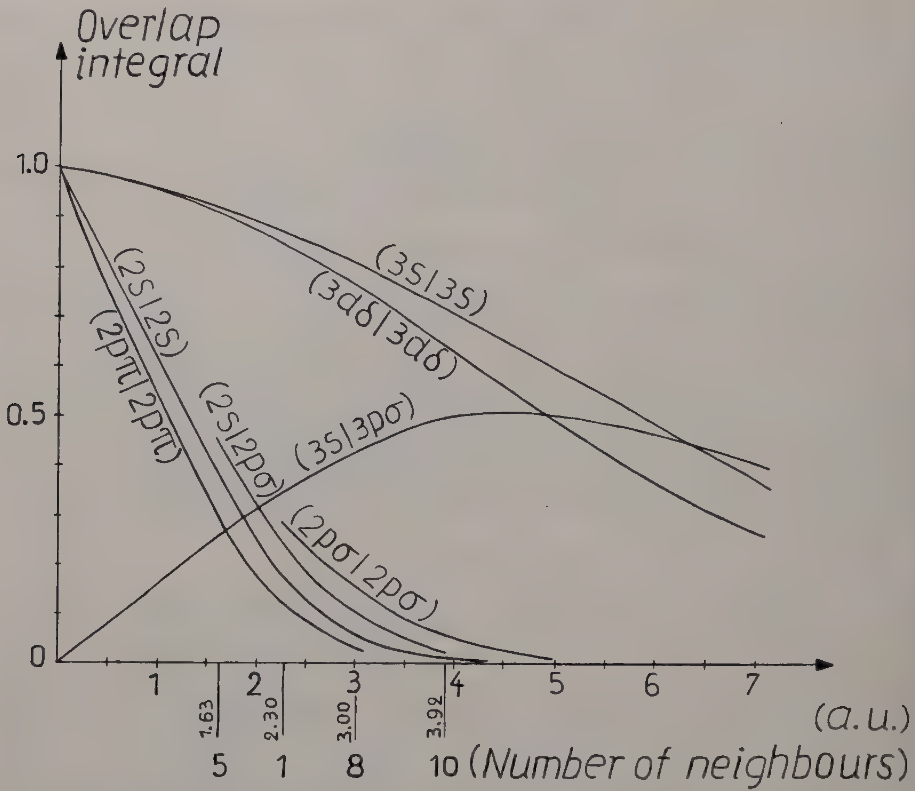

Fig. 4. Some overlap integrals given as functions of half the distance between the two centres. For the nearest neighbours in the crystal the actual half distances and the corresponding number of neighbours have been added to the diagram.

This approximation is rather good for small overlap integrals. Integrals of the type (45) occur in sums over B apart from B′ and B″. Since all the B atoms are equivalent in the crystal lattice, we also have the identity,

$$\frac{1}{2}\sum_{\substack{B\neq B'\\ B\neq B''}}\left(\frac{1}{r_{BB'}}+\frac{1}{r_{BB''}}\right)=\sum_{B\neq B_0}\frac{1}{r_{BB_0}}-\frac{1}{r_{B'B''}}. \tag{46}$$

Thus, since the effective charges (53) connected with (45) are approximately independent of the individual atomic orbitals, these integrals would vanish when taken together with the corresponding contribution from the fixed charges in (38) for the case $\lambda = 0$. In other cases there is left a term with the factor $-1 + 1/(1+\lambda/9) = -\lambda/(9+\lambda)$ for the sum of the integrals of the type (45). The corresponding thing is valid for the three-centre integrals containing $1/r_M$. Denoting the inter-atomic distances B_0B and B_0M with R_b and R_m respectively, we find in our approximation:

$$\begin{aligned} h_0 &= \langle \mathrm{B}_0 | h | \mathrm{B}_0 \rangle \\ &= C_0 - Z_0\, B_0 - \sum_{b \neq 0}^{(24)} Z_b \left(D_b - \frac{1}{1+\lambda/9} \frac{A_0}{R_b} \right) - \\ &\qquad - 2\lambda \sum_{m}^{(8)} \left(D_m - \frac{1}{1+\lambda/9} \frac{A_0}{R_m} \right) + \frac{1}{18+2\lambda} (I + \lambda^2 \varepsilon_{\mathrm{R}})\, A_0, \end{aligned} \tag{47}$$

$$\begin{aligned} h_b &= \langle \mathrm{B}_0 | h | \mathrm{B} \rangle \\ &= C_b - \bar{Z}_b\, B_b + \left\{ \frac{\bar{Z}_b}{R_b} + \frac{1}{18+2\lambda} \left(2\lambda \sum_{b'}^{(24)} \frac{Z_{b'}}{R_{b'}} - 4\lambda^2 \sum_{m}^{(8)} \frac{1}{R_m} + I + \lambda^2 \varepsilon_{\mathrm{R}} \right) \right\} A_b, \quad (b \neq 0). \end{aligned} \tag{48}$$

The effective charges must have different values for the different integrals occurring in (47) and (48). For one-centre integrals of the type B_0 in (44) the notation Z_0 is used instead of $Z_{\mathrm{B}}^{\mathrm{eff}}$. For ionic integrals of the type D_b in (44) and of the type (45) the notation Z_b and for integrals of the type B_b in (44) the notation $\bar{Z}_b$ have been used for the effective charge. According to Fischer-Hjalmars [11], we can use

$$Z_0(\nu) = 5 - \frac{\int \varphi_\nu^* [\varrho(r)/r]\, \varphi_\nu\, d\tau}{\int \varphi_\nu^* (1/r)\, \varphi_\nu\, d\tau} = 1 - \frac{\lambda}{3} + \frac{\langle g(r) \rangle}{\langle 1/r \rangle} \tag{49}$$

for one-centre integrals, containing equal atomic orbitals φ_ν, since B has the nuclear charge 5. In this expression, $\varrho(r)$ is an approximate, spherically symmetrical charge density function for the electron cloud at a certain atom B_0, consisting of all the $4 + \lambda/3$ electrons, which are not concerned by the atomic orbital φ_ν, and r is the radius vector from B_0. Thus, in order to determine these effective charges, it is necessary to compute only some simple one-centre two-electron integrals. According to Slater [12], it is convenient to introduce some additional averaged "exchange charge density", but this has been neglected here. Thus, we are working in the Hartree approximation. The reliability of this method depends on the orbitals used very markedly. Here, the $1s$ orbitals have been supposed to be completely filled and all the other electrons—except the one under consideration—have been supposed to occupy $2s$ and $2p$ orbitals only. Using (49) the screening function, $g(r)$, thus simply is found according to

$$r\, g(r) = 2(1 + \zeta_{1s}) \exp(-2\zeta_{1s}\, r) + s f(\zeta_{2s}\, r) + p f(\zeta_{2p}\, r), \tag{50}$$

where $$f(\zeta r) = (1 + \tfrac{3}{2} \zeta r + \zeta^2 r^2 + \tfrac{1}{3} \zeta^3 r^3) \exp(-2\zeta r).$$

The coefficient s occurring in (50) is the number of $2s$ orbitals and p is the number of $2p$ orbitals in the electron cloud, and the total number is $s + p = 2 + \lambda/3$. The numerical constants ζ occurring in (50) are the orbital exponents of the Slater atomic orbitals. For the orbitals used in the LM approximation these are given by

$$\left. \begin{aligned} &\zeta_{2s} = 1.34, \quad \zeta_{2p} = 1.205, \ [13]; \\ &\zeta_{1s} = 4.7, \quad \zeta_{3s} = \zeta_{3p} = 0.433, \quad \zeta_{3d} = 0.333, \ [14]. \end{aligned} \right\} \tag{51}$$

The "diagonal" integrals in (49) apparently also depend on the different atomic orbitals φ_ν. For "non-diagonal" one-centre integrals there has been used a mean value for the effective charges:

$$Z_0(\nu', \nu'') = \tfrac{1}{2}[Z_0(\nu') + Z_0(\nu'')]. \tag{52}$$

For the two-centre ionic integrals of the type D_b in (44), Z_B^{eff} is approximately independent of the different orbitals occurring in the integrals. Thus, it depends only on the distance between the different centres of the integrals. In this case the following approximation has been used:

$$Z_b = 5 - \frac{\langle B_0 | \varrho(B)/r_B | B_0 \rangle}{\langle B_0 | 1/r_B | B_0 \rangle} = -\frac{\lambda}{3} + \frac{\langle B_0 | g(r_B) | B_0 \rangle}{\langle B_0 | 1/r_B | B_0 \rangle} \approx -\frac{\lambda}{3} + R_b\, g(R_b). \tag{53}$$

Here $\varrho(B)$ is the charge density of all the $5 + \lambda/3$ electrons at B, r_B is the distance between the point of integration and the nucleus B and g is the screening function given by (50) with $s + p = 3 + \lambda/3$. Since the atomic orbitals are localized to B_0, this approximation is rather good, at least for orbitals of the L shell. For large distances Z_b tends towards $-\lambda/3$, as is seen from (53) and (50). In this case the contribution from $(1s)$ orbitals in g is negligible. The expression (53) for Z_B^{eff} has been used also for integrals of the type (45) and for the corresponding nuclear energy integrals.

The values of Z_B^{eff} are given in Table 6 for $\lambda = 0$ and $\lambda = 1$ and for different distances R_b. The influence of the chosen ratio p/s on these values is rather small, since ζ_{2s} and ζ_{2p} according to (51) are nearly equal to each other. In Table 6, s has been chosen equal to $2(2 + \lambda/3)/(3 + \lambda/3)$. For integrals of the type B_b in (44), $Z_B^{\text{eff}} = \bar{Z}_B$ has been chosen arithmetically intermediate to (52) and (53). Hence it is dependent on all the quantities $\varphi_{\nu'}$, $\varphi_{\nu''}$ and R_b in this case.

Table. 6. Effective charges Z_B^{eff} in a.u. (see eq. (49) and (53)).

Orbital φ_ν	Z_0		Distance R_b (a.u.)	Z_b	
	$\lambda = 0$	$\lambda = 1$		$\lambda = 0$	$\lambda = 1$
$2s$	1.5856	1.3540	3.2502	0.0398	−0.2885
$2p$	1.5054	1.2607	4.5964	0.0032	−0.3297
$3s$, $3p$	1.0082	0.6765	6.0056	0.0002	−0.3331
$3d$	1.0028	0.6700	7.8466	0.0000	−0.3333

6. Calculation and transformation of the energy integrals

The two-centre integrals in (44) have been solved by use of an automatic program constructed by the present author for the electronic computer Besk [15]. However, in this program the occurring orbitals are referred to parallel coordinate systems with common z axes. Thus, it is necessary to perform coordinate transformations for the orbitals of both the centres (see Fig. 5). Under such transformations the s functions are invariant and the p functions are transformed as vector components. The elements of the five-dimensional transformation matrix $\mathbf{A}$ for the transformation $\mathbf{d}(\bar{\mathbf{x}}_B) = \mathbf{d}(\mathbf{x}_B)\mathbf{A}$ of the d orbitals are given in Table 7. These elements are expressed in the elements of the matrix $\mathbf{B}$ for the rotation $\bar{\mathbf{x}}_B = \mathbf{B}\mathbf{x}_B$ of the local coordinate system

Table 7. Transformation elements A_{ij} of the d orbitals $\bar{d}_j = \sum_{i=1}^{5} d_i A_{ij}$ for orthogonal coordinate transformations, $\bar{x}_m = \sum_{n=1}^{3} B_{mn} x_n$, x_n denoting x, y, z.

$d_i \diagdown \bar{d}_j$	$\bar{d}_{x^2-y^2}$	$\bar{d}_{xy}$	$\bar{d}_{zx}$	$\bar{d}_{zy}$	$\bar{d}_{z^2}$
$d_{x^2-y^2}$	$\frac{1}{2}(B_{11}^2 - B_{12}^2 + B_{22}^2 - B_{21}^2)$	$B_{11}B_{21} - B_{12}B_{22}$	$B_{11}B_{31} - B_{12}B_{32}$	$B_{21}B_{31} - B_{22}B_{32}$	$\frac{1}{2}\sqrt{3}\,(B_{31}^2 - B_{32}^2)$
d_{xy}	$B_{11}B_{12} - B_{21}B_{22}$	$B_{11}B_{22} + B_{12}B_{21}$	$B_{11}B_{32} + B_{12}B_{31}$	$B_{21}B_{32} + B_{22}B_{31}$	$\sqrt{3}\,B_{31}B_{32}$
d_{zx}	$B_{11}B_{13} - B_{21}B_{23}$	$B_{11}B_{23} + B_{13}B_{31}$	$B_{11}B_{33} + B_{13}B_{31}$	$B_{21}B_{33} + B_{23}B_{31}$	$\sqrt{3}\,B_{31}B_{33}$
d_{zy}	$B_{12}B_{13} - B_{22}B_{23}$	$B_{12}B_{23} + B_{13}B_{22}$	$B_{12}B_{33} + B_{13}B_{32}$	$B_{22}B_{33} + B_{32}B_{23}$	$\sqrt{3}\,B_{32}B_{33}$
d_{z^2}	$-\frac{1}{2}\sqrt{3}(B_{11}^2 + B_{12}^2 - B_{22}^2 - B_{21}^2)$	$-\sqrt{3}\,(B_{11}B_{21} + B_{12}B_{22})$	$-\sqrt{3}\,(B_{11}B_{31} + B_{12}B_{32})$	$-\sqrt{3}\,(B_{21}B_{31} + B_{22}B_{32})$	$\frac{1}{2}(3\,B_{33}^2 - 1)$

at B. Here $\mathbf{x}_\mathrm{B}$ is a column matrix of the position vector with the point B as origin, and $\mathbf{d}$ is a row matrix with the five d orbitals as elements. By use of these transformations we easily find the transformation of the energy integrals. For integrals consisting of d orbitals only, for example, we can introduce the five-dimensional quadratic matrix

$$\mathbf{D} = \int \mathbf{d}^\dagger(\mathbf{x}_{\mathrm{B}'})\, h\, \mathbf{d}(\mathbf{x}_{\mathrm{B}''})\, d\tau. \tag{54}$$

The transformation formula is in this case

$$\overline{\mathbf{D}} = \mathbf{A}'^\dagger \mathbf{D} \mathbf{A}''. \tag{55}$$

As has been pointed out earlier, the integrals have been calculated for the 24 nearest B neighbours and the 8 nearest M neighbours of a given B atom. The transformation matrices $\mathbf{B}$ are similar for many of these integrals, but there are still many different types (see Fig. 5). The largest distance B–B, occurring in the computed integrals, is equal to the cell width, which is the same as the shortest distance M–M in the crystal. The largest distance B–M occurring in these integrals is somewhat larger. In the expansion ε_R, occurring in (38), however, interaction between charges at much larger distances has been taken into account, but this does only concern point charges.

In Table 8 numerical values of some of the "diagonal" energy integrals of the types (47) and (48) are given. The directions B′–B″, symbolized by the index b, are given by Fig. 5. The coordinate systems for the respective B centres are those given by Fig. 2, used for all the sites. This means, that "equally situated" B atoms in different sites have parallel coordinate systems. The notation "diagonal" used in Table 8 concerns the different types of atomic orbitals. However, this notation is somewhat arbitrary, since the "diagonality" also depends on the way of choosing the coordinate systems. In any case, the given elements might be representative also for the order of magnitude of the many "non-diagonal" elements.

From Table 8 it is seen that integrals connecting orbitals of the L shell are rather small at the largest distance B–B, which has been taken into consideration, but many of the M shell integrals are here still considerable. Thus, in order to get more reliable

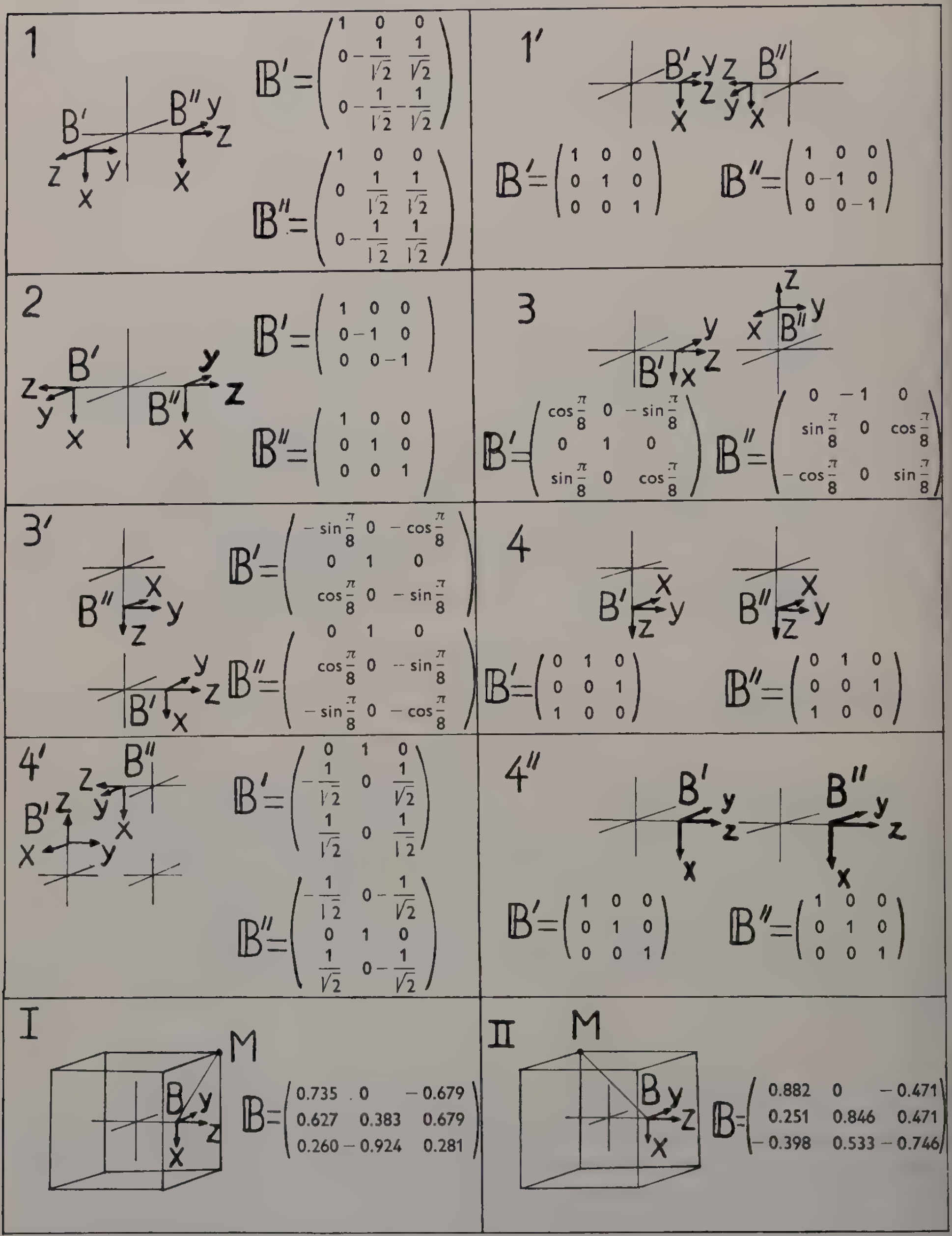
1
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}1&0&0\\0&-\frac{1}{\sqrt2}&\frac{1}{\sqrt2}\\0&-\frac{1}{\sqrt2}&-\frac{1}{\sqrt2}\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}1&0&0\\0&\frac{1}{\sqrt2}&\frac{1}{\sqrt2}\\0&-\frac{1}{\sqrt2}&\frac{1}{\sqrt2}\end{pmatrix}$
1′
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}$
2
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$
3
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}\cos\frac{\pi}{8}&0&-\sin\frac{\pi}{8}\\0&1&0\\\sin\frac{\pi}{8}&0&\cos\frac{\pi}{8}\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}0&-1&0\\\sin\frac{\pi}{8}&0&\cos\frac{\pi}{8}\\-\cos\frac{\pi}{8}&0&\sin\frac{\pi}{8}\end{pmatrix}$
3′
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}-\sin\frac{\pi}{8}&0&-\cos\frac{\pi}{8}\\0&1&0\\\cos\frac{\pi}{8}&0&-\sin\frac{\pi}{8}\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}0&1&0\\\cos\frac{\pi}{8}&0&-\sin\frac{\pi}{8}\\-\sin\frac{\pi}{8}&0&-\cos\frac{\pi}{8}\end{pmatrix}$
4
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}0&1&0\\0&0&1\\1&0&0\end{pmatrix}$
4′
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}0&1&0\\-\frac{1}{\sqrt2}&0&\frac{1}{\sqrt2}\\\frac{1}{\sqrt2}&0&\frac{1}{\sqrt2}\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}-\frac{1}{\sqrt2}&0&-\frac{1}{\sqrt2}\\0&1&0\\\frac{1}{\sqrt2}&0&-\frac{1}{\sqrt2}\end{pmatrix}$
4″
B′ B″ x y z
$\mathbb{B}'=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$
$\mathbb{B}''=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}$
I
M B x y z
$\mathbb{B}=\begin{pmatrix}0.735&0&-0.679\\0.627&0.383&0.679\\0.260&-0.924&0.281\end{pmatrix}$
II
M B x y z
$\mathbb{B}=\begin{pmatrix}0.882&0&-0.471\\0.251&0.846&0.471\\-0.398&0.533&-0.746\end{pmatrix}$

Fig. 5. Some distances in the crystal, denoted by $b = 1, 1', 2, \ldots$ for the two-centre integrals (44), and the corresponding matrices for the coordinate transformations of each centre. The given matrices, $\mathbf{B}'$ and $\mathbf{B}''$ can be used for transforming the occurring two-centre integrals into a form suitable for computation by Besk (cf. Table 7). For I and II the transformations of only the B coordinate systems are given. These are useful for ionic integrals of the type D_m in (44).

Table 8. Some "diagonal" elements, $\langle\varphi|h_b|\varphi\rangle$ of (47) and (48). These are energy integrals connecting different atoms (cf. Fig. 5).

$\varphi \diagdown b$	0	1	1′	2	3	4
$2\,s$	−0.663	−0.342	−0.342	−0.149	−0.053	−0.012
$2\,p_x$	−0.125	−0.170	−0.170	−0.075	0	−0.006
$2\,p_y$	−0.125	0.133	0.170	0.075	0	0.034
$2\,p_z$	−0.125	−0.133	−0.097	−0.146	0.043	−0.006
$3\,s$	−0.115	−0.430	−0.430	−0.386	−0.344	−0.293
$3\,p_x$	−0.124	−0.392	−0.392	−0.340	0	−0.228
$3\,p_y$	−0.124	0.035	0.392	0.340	0	−0.007
$3\,p_z$	−0.124	−0.035	0.323	0.221	0.060	−0.228
$3\,d_{z^2}$	0.131	0.148	−0.301	−0.204	0.055	−0.184
$3\,d_{zx}$	0.059	−0.029	0.316	0.230	0	−0.230
$3\,d_{zy}$	0.059	0.319	−0.316	−0.230	0	−0.044
$3\,d_{xy}$	−0.018	0.029	0.374	0.328	0.049	−0.044
$3\,d_{x^2-y^2}$	0.133	−0.188	−0.374	−0.333	0.144	−0.090

results, it might seem that neighbours at even larger distances ought to have been taken into account. However, this would probably be rather meaningless, since, for example, the approximations in (45) and (53) are very rough for orbitals of the *M* shell.

7. Discussion of the methods

As we have seen, there are many different approximations implied in the methods used in the present work. First of all, the chosen types of orbitals might be discussed.

Certainly it is questionable whether it is applicable at all to use one-electron orbitals in crystals of the present type of structure. The answer to this question can only be given by the reasonableness of the found results. When working in the one-electron approximation it might be put in question if it is suitable to use Slater atomic orbitals localized to the different atoms in each site, i.e. the MO treatment. When using these orbitals it is maybe not convenient to break off the set of atomic orbitals already with the *M* shell. It is not evident indeed, that even more excited atomic orbitals need not be taken into account in order to describe the electron distribution of the total crystal. Thus maybe the set of atomic orbitals is no good starting point for the expansions of the site orbitals. However, it is difficult to find a better practical way of approximation.

The cellular method would probably reduce the computations somewhat, but it has not been used in the present work. Since this method is not very accurate for the excited states, it would probably be of less accuracy than the method used for MB_6 in the present paper, when we are looking for the contribution also of *M* shell orbitals. Furthermore, the cellular method implies the use of a rather complicated unit cell for every single B atom in the MB_6 crystal. Von der Lage and Bethe have applied the cellular method to sodium [16], which also belongs to the cubic point symmetry group O_h. These authors have constructed the eigenfunctions of the approximately spherically symmetrical one-electron Hamiltonian operator for the cubic unit cell in terms of so called "Kubic Harmonics", i.e. linear combinations of spherical harmonics suitable for the cubic symmetry. The origin of the Kubic Harmonics is the centre of the unit cell. In a very rough application of the cellular method to the present problem, these Kubic Harmonics might be chosen as a starting point in using the total cubic cell as unit cell, since the symmetry of the site structure might make it reasonable to use spherically symmetrical potentials with the origin at the centre for every cubic cell. However, the bonds between the different atoms within a site do not come to explicit expression by use of this method. In the present work the orbitals corresponding to these Kubic Harmonics are hybridized Slater atomic orbitals localized to the octahedron corners inside the cell (see Table 5).

A strict application of the cellular method to close-packed hexagonal lattices, where there are two atoms inside every cell has recently been performed by Altmann [17]. He also showed that the symmetry properties of the basic orbitals for the total space group $\mathfrak{G}'$ of the crystal can be found for certain **k**-values[1] by using the irreducible representations of the point symmetry group, $\mathfrak{G}$. This is in agreement with the results of section 3 in the present paper. The whole computing process of [17] has also been programmed for an electronic computer. In the present problem it has only been practically possible to use an electronic computer for certain parts of the calculations.

Probably the most dubious approximation used in the present work is the rough estimation of the electronic Coulomb energy by use of effective charges. However, the actual problem of computing all the two-electron Coulomb energy integrals and of taking these into consideration in the total energy variation problem would be an enormous task. In spite of using an electronic computer for part of the numerical calculations, it is scarcely likely that this might be finished within reasonable time.

Furthermore, it is a rather bad approximation to cut off the sums over the sites as early as has been made in the present work, where atom neighbours up to the distance between two metal atoms have been considered. On the other hand, it is certainly no idea taking integrals for larger distances into account, not only since it would be a great deal of extra work, but also since the orbitals of the electrons belonging to the metal atoms then ought to be considered explicitly. For the L shell orbitals, the approximation of neglecting the distant sites probably gives a difference from the total sum over all the sites with only a few percents. For the M shell orbitals, however, the last term taken into account in the expansion is almost of the same order of magnitude as the whole sum of the preceding terms. This is very sensitive for the overlap integrals, since for certain points in the wave vector space the overlap matrices of the secular equations are not positively definite on account of the early cut off of the site neighbours for the M shell orbitals. This caused some trouble when using the electronic computer Besk, since the program for secular equations requires that the overlap matrices are positively definite. Thus the contribution of the excited orbitals to the electron distribution can only be found qualitatively. As is seen in the next section, however, the energy eigenvalues are generally not very much affected by this approximation.

Finally, we will discuss the orbital exponents (51) occurring in the Slater atomic orbitals. According to more recent investigations the orbital exponents of the excited orbitals should be chosen larger. This might change the results somewhat. However, it does not affect the L approximation, and since the influence of the excited orbitals on account of the many approximations in the present work can at any rate only be described qualitatively, this may not be taken too seriously. Furthermore, since the valence electrons in the ground state of boron only occupy the L shell, it still seems to be well-grounded to use almost complete screening for the M shell orbitals. As a matter of fact, the results found in [2] yielded orbital exponents lying between 0.23 and 0.36 for the excited $3d$ orbitals in the different kinds of metal borides (cf. the introduction). For CaB_6 the value $\zeta_{3d} = 0.323$ was found, which is very close to the value given in (51).

---

[1] These **k**-values are those for which the space groups $\mathfrak{G}'$ and $\mathfrak{G}^{\mathbf{k}}$ are identical, where $\mathfrak{G}^{\mathbf{k}}$ is the subgroup of $\mathfrak{G}'$ that leaves the function $\exp(i\,\mathbf{k}\,\mathbf{n})$ occurring in the Bloch orbitals invariant.

The low values of these orbital exponents certainly depend upon the ionization of the metal atoms, since the valence electrons of the metal can be considered to occupy the excited M shell orbitals of boron. Thus, for these orbitals there are $4\frac{1}{3}$ K and L electrons almost completely screening a B nucleus, which has the nuclear charge 5. This corresponds to an effective charge somewhat larger than 2/3. Thus the orbital exponent for the $3d$ orbitals will be about 2/9 or a little more, in consistence with the results of [2]. As will be seen in the next section, the results of the present investigation also confirm that the valence electrons of the metal really can occupy bonding site orbitals mainly on account of the excited M shell orbitals.

8. Electron distribution and energy bands

The elements of the secular equations have been calculated for the following special points in the wave vector space:

$$\left.\begin{aligned} &\mathbf{k}_1=(0,0,0),\quad \mathbf{k}_2=(\pm\pi,0,0),\quad \mathbf{k}_3=\begin{cases}(0,\pm\pi,0),\\(0,0,\pm\pi),\end{cases}\\ &\mathbf{k}_4=\begin{cases}(\pm\pi,\pm\pi,0),\\(\pm\pi,0,\pm\pi),\end{cases}\quad \mathbf{k}_5=(0,\pm\pi,\pm\pi),\quad \mathbf{k}_6=(\pm\pi,\pm\pi,\pm\pi).\end{aligned}\right\}\qquad(56)$$

Points in the $\mathbf{k}$ space giving identical energies and electron distribution have been put together under the same notation in (56). The plus or minus sign can be arbitrarily taken for every component. The directions of the y- and z-axes of the coordinate system in (56) are chosen to be the two equivalent directions for the basic orbital in question. The corresponding secular equations have been solved separately for all the nonvanishing site orbitals in the L approximation. The energy eigenvalues and the electron distribution of the bonding site orbitals in this approximation are given in Table 9 and Table 10 resp. Here the site orbitals are denoted by a preceding figure in addition giving the number of the root of the corresponding secular equation. The site orbitals are supposed to be doubly occupied on account of the two spin orientations and they are ordered with respect to decreasing bond strengths. But, as is seen from Table 9, the orbital $1t_{1u}$ has only one bonding direction in the table. Thus, it cannot be completely filled. Also some of the other bonding orbitals, namely $1e_g$, $1t_{2g}$ and $2a_{1g}$, give only partly filled bands. The orbitals $1t_{2u}$, $2t_{1u}$, $1t_{1g}$ and $2e_g$ are antibonding in all directions. In roughly counting the ratio of the number of $\mathbf{k}$ points with negative energies and the total number of $\mathbf{k}$ points in Table 9 as a factor for the occupation numbers, we see that there is room only for about 18 bonding electrons of every site in the L approximation. However, on account of the ionization of the bivalent metal atoms, there are 20 valence electrons available for the bonding orbitals of every site. Thus the L approximation does not give so many strongly bonding orbitals as is necessary to describe all the 20 valence electrons of the site.

Table 9. Energy eigenvalues $\varepsilon_{\mathbf{k}}$ of the secular equations in the L approximation.

Basic site orbital	Space degeneracy l_j	Degree of the secular equ.	$\varepsilon_{\mathbf{k}}$ for certain points in the **k** space						Conduction bands[1]
			$(0, 0, 0)$	$(\pi, 0, 0)$	$(0, \pi, 0)$ $(0, 0, \pi)$	$(\pi, \pi, 0)$ $(\pi, 0, \pi)$	$(0, \pi, \pi)$	(π, π, π)	
$1\,a_{1g}$	1	2	−0.815	−0.805	−0.805	−0.788	−0.788	−0.753	
$1\,t_{1u}$	3	3	0.060	2.67	12.8	1.83	−0.706	1.99	x
$3\,t_{1u}$	3	3	−0.532	−0.627	−0.466	−0.696	−0.377	−0.491	
$1\,e_g$	2	2	−0.553	0.694	−0.082	−0.436	−0.531	−0.423	x
$1\,t_{2g}$	3	1	0.068	−0.333	−0.334	−0.201	0.099	−0.222	x
$2\,a_{1g}$	1	2	−0.184	−0.138	−0.138	0.022	0.022	1.286	x
$1\,t_{2u}$	3	1	0.290	0.501	0.852	0.055	0.028	0.663	Totally anti-bonding
$2\,t_{1u}$	3	3	1.24	0.275	2.23	0.077	0.033	0.221	
$1\,t_{1g}$	3	1	1.65	0.543	0.346	0.809	2.24	0.799	
$2\,e_g$	2	2	2.01	3.91	1.70	2.83	3.73	1.67	

[1] When conduction bands occur, this has been marked with an x.

Table 10. Eigenvectors of the secular equations for the bonding orbitals in the L approximation.

Basic site orbital	Atomic orbital φ_ν (¹)	Coefficients C_ν of the atomic orbitals for different points in the **k** space					
		$(0, 0, 0)$	$(\pi, 0, 0)$	$(0, \pi, 0)$ $(0, 0, \pi)$	$(\pi, \pi, 0)$ $(\pi, 0, \pi)$	$(0, \pi, \pi)$	(π, π, π)
$1\,a_{1g}$	$2\,s$	0.996	0.991	0.991	0.989	0.989	0.993
	$2\,p\,\sigma$	0.092	0.130	0.130	0.147	0.147	0.119
$1\,t_{1u}$	$2\,s$	0.925	0.817	0.881	0.805	0.999	0.719
	$2\,p\,\sigma$	−0.101	−0.187	−0.193	−0.461	0.001	0.579
	$2\,p\,\pi$	−0.367	0.546	−0.432	−0.374	−0.038	−0.384
$3\,t_{1u}$	$2\,s$	0.980	0.939	0.974	0.999	−0.454	0.865
	$2\,p\,\sigma$	0.035	0.228	0.005	0.034	−0.014	−0.003
	$2\,p\,\pi$	0.195	0.259	0.225	0.018	0.891	0.502
$1\,e_g$	$2\,s$	0.984	0.991	0.964	0.952	0.977	0.964
	$2\,p\,\sigma$	0.180	0.133	0.266	0.307	0.214	0.267
$1\,t_{2g}$	$2\,p\,\pi$	1	1	1	1	1	1
$2\,a_{1g}$	$2\,s$	0.152	0.336	0.336	0.549	0.549	0.749
	$2\,p\,\sigma$	0.988	0.942	0.942	0.836	0.836	0.662

(¹) "Atomic orbital" here means the basic site orbitals of Table 5 with only one type of atomic orbital. The notation σ in this table corresponds to z in Table 5 and π corresponds to x and y.

In the LM approximation, however, there is a sufficient number of strongly bonding site orbitals. This is seen from Table 11 and Fig. 6, which give energy eigenvalues and energy bands for some bonding orbitals resp. The corresponding electron distribution is given by Table 12. The coefficients C_ν in Tables 10 and 12 are those of (19).

Table 11. Energy eigenvalues $\varepsilon_{\mathbf{k}}$ of the secular equations in the *LM* approximation.

Basic site orbital	Space degeneracy l_j	Degree of the secular equ.	$\varepsilon_{\mathbf{k}}$ for certain points in the **k** space						Conduction bands[1]
			$(0, 0, 0)$	$(\pi, 0, 0)$	$(0, \pi, 0)$ $(0, 0, \pi)$	$(\pi, \pi, 0)$ $(\pi, 0, \pi)$	$(0, \pi, \pi)$	(π, π, π)	
$1\,a_{1g}$	1	5	−1.013	−0.861	−0.861				
$1\,t_{1u}$	3	8	0.657				−0.728		x
$1\,e_g$	2	6	−0.57		−0.38			−0.45	(x)
$3\,t_{1u}$	3	8	−0.504				−0.345		
$6\,t_{1u}$	3	8	−0.391				−0.421		
$3\,a_{1g}$	1	5	−0.382	−0.388	−0.388				
$3\,t_{2g}$	3	3	−0.364		0.561			−0.273	x
$1\,t_{2g}$	3	4	0.029	−0.350	−0.349			−0.177	x
$5\,e_g$	2	6	−0.34					−0.284	
$4\,e_g$	2	6	−0.34					−0.2	
$4\,t_{1u}$	3	8	−0.312				−0.247		
$4\,t_{2g}$	3	4	1.28		−0.320		0.5	0.4	x
$2\,t_{2g}$	3	4	−0.253		0.037	0.066		−0.311	x
$2\,t_{1g}$	3	3	−0.3		−0.253				
$5\,t_{1u}$	3	8	1.99				−0.294		x
$6\,e_g$	2	6	−0.206		−0.274				
$4\,a_{1g}$	1	5	−0.263						
$8\,t_{1u}$	3	8	−0.227				0.446		x
$3\,e_g$	2	6			−0.179				
$2\,a_{1g}$	1	5	−0.161	−0.064	−0.064				(x)
$3\,t_{1g}$	3	3			−0.147			−0.160	
$5\,a_{1g}$	1	5	0.038	−0.142	−0.142				x
$3\,t_{2u}$	3	4				−0.127			
$7\,t_{1u}$	3	8	0.051				0.020		Totally anti-bonding
$1\,t_{2u}$	3	4				0.082			
a_{2u}	1	1	5.2			0.3		0.1	
$1\,t_{1g}$	3	3	1.2		0.4			0.7	
e_u	2	1	0.5						
$4\,t_{2u}$	3	4	2.9		0.6				
$2\,e_g$	2	6	4.2		2.5			2.9	
$2\,t_{1u}$	3	8	3.5				2.8		
a_{2g}	1	1	11.6						
$2\,t_{2u}$	3	4				13.5			

[1] See the note under Table 9. The notation (x) means that the conduction bands can be seen only from Table 9.

The explicit expression of the site orbitals are finally found by using Table 5. As we see from Table 12, the distribution of *d* orbital electrons is remarkably essential also for the most stable configurations in good agreement with the supposition in [2].

On account of the uncertainties discussed in the preceding section for the *M* shell

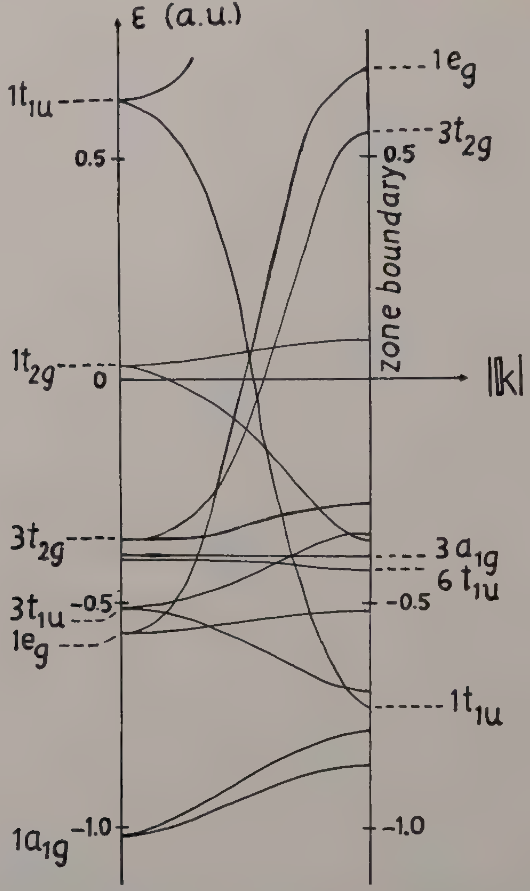

Fig. 6. Regions of the energy bands for some of the bonding site orbitals. Bands for orbitals with large contribution from the M shells (e.g. $3t_{2g}$, $3a_{1g}$ and $6t_{1u}$) are rather uncertain.

orbitals, it is not possible to find the solutions of the secular equations for some of the directions in the **k** space without working out more terms in the expansion over the site neighbours. Hence there is some open space in the tables. However, in spite of the somewhat incomplete and inaccurate values for the excited atomic orbitals, Table 11 constitutes a good complement to Table 9. As is seen, the inclusion of excited orbitals does not disorder the energies of the orbitals in Table 9. This only gives a little lowering of the lowest lying levels. The main point here is, however, that some of the strongly bonding site orbitals, which do not excist in the L approximation, namely for example $6t_{1u}$ and $3a_{1g}$ are stronger bonding than several of the weakest bonding orbitals in the L approximation. This means, that in the LM approximation there is a sufficient number of strongly bonding orbitals for the 20 valence electrons of every site.

Table 12. Eigenvectors of the secular equations for the strongest bonding orbitals in the LM approximation.

Basic site orbital	Atomic orbital φ_ν (¹)	Coefficients C_ν of the atomic orbitals for different points in the **k** space				
		$(0, 0, 0)$	$(\pi, 0, 0)$	$(0, \pi, 0)$ $(0, 0, \pi)$	$(0, \pi, \pi)$	(π, π, π)
$1\,a_{1g}$	$2\,s$	0.917	0.923	0.923		
	$2\,p\,\sigma$	0.145	0.097	0.097		
	$3\,s$	−0.173	−0.107	−0.107		
	$3\,p\,\sigma$	0.032	0.246	0.246		
	$3\,d\,\sigma$	−0.327	−0.258	−0.258		
$1\,t_{1u}$	$2\,s$	0.882			0.953	
	$2\,p\,\sigma$	−0.161			−0.031	
	$2\,p\,\pi$	−0.313			−0.007	
	$3\,s$	−0.257			−0.134	
	$3\,p\,\sigma$	0.041			0.185	
	$3\,p\,\pi$	0.043			−0.000	
	$3\,d\,\sigma$	0.161			0.125	
	$3\,d\,\pi$	0.051			0.153	
$1\,e_g$	$2\,s$	0.948		0.796		0.916
	$2\,p\,\sigma$	0.282		0.073		0.325
	$3\,s$	−0.146		−0.142		−0.216
	$3\,p\,\sigma$	−0.005		0.505		−0.044
	$3\,d\,\sigma$	−0.020		−0.274		0.021
	$3\,d\,\delta$	−0.013		0.106		0.074
$3\,t_{1u}$	$2\,s$	0.919			0.132	
	$2\,p\,\sigma$	0.045			−0.255	
	$2\,p\,\pi$	0.321			0.584	
	$3\,s$	0.036			−0.506	
	$3\,p\,\sigma$	0.036			−0.104	
	$3\,p\,\pi$	0.134			−0.310	
	$3\,d\,\sigma$	−0.107			0.409	
	$3\,d\,\pi$	−0.132			0.215	
$6\,t_{1u}$	$2\,s$	−0.196			−0.418	
	$2\,p\,\sigma$	−0.081			0.079	
	$2\,p\,\pi$	−0.519			0.757	
	$3\,s$	−0.436			−0.354	
	$3\,p\,\sigma$	0.624			0.068	
	$3\,p\,\pi$	0.252			0.293	
	$3\,d\,\sigma$	−0.180			0.047	
	$3\,d\,\pi$	−0.105			−0.167	
$3\,a_{1g}$	$2\,s$	−0.455	−0.337	−0.337		
	$2\,p\,\sigma$	0.238	0.308	0.308		
	$3\,s$	0.718	0.797	0.797		
	$3\,p\,\sigma$	−0.465	−0.376	−0.376		
	$3\,d\,\sigma$	0.064	0.119	0.119		

(¹) The symbols σ, π, δ of the d orbitals correspond to the orbitals of the types $3d_{z^2}$, $3d_{zx}$ and $3d_{zy}$, $3d_{x^2-y^2}$, resp., in Table 5. See also the note under Table 10.

Furthermore, it is seen from Table 9 and Fig. 6, that the doubly degenerate orbital $1e_g$ is strongly antibonding for the **k** vector $(\pi, 0, 0)$, which is perpendicular to the plane containing the $2s$ and $2p$ orbitals (see Fig. 3). These energy bands are thus only partly filled, implying metallic conductivity. Certainly, these conduction bands will be a little disturbed on account of the fact that the secular equation is not exactly factorizable in this direction of the wave vector space (see section 3). But, the occurrence of these conduction bands depends mainly on the fact that we are working outside the tight-binding approximation. Furthermore, the most distant neighbours taken into account only modify the energies with about one per cent. Thus, the existence of these bands seems to be quite certain. An interesting point in this connection is, that for sodium the electrons also are essentially free in the corresponding direction [16]. As is seen from Table 11, similarly also $1t_{1u}$ and the orbitals of type t_{2g} are partly antibonding.

9. Discussion of the results

The results given in the previous section are partly in contradiction to the results found by Longuet-Higgins and de V. Roberts [3], who have found a closed shell structure for MB_6 without any conduction bands. The experimentally found metallic conductivities of the metal borides with bivalent metal atoms have been explained by these authors as effects caused by impurities or lattice defects of the crystals. Of course, this cannot really be disproved, but the results of the present investigation show a more natural way of explaining the occurrence of these conductivities, since several of the most strongly bonding site orbitals show up conduction bands.

The sequence of the strongly bonding site orbitals found by the present method in the L approximation is mainly in accordance with the results found by [3]. In [3] the stability has been explained by use of only L shell orbitals. The present investigation shows, however, that also M shell orbitals are necessary for explaining the stability of the crystal, since some of the site orbitals, which only exist in the LM approximation, are more strongly bonding than the weakest bonding orbitals in the L approximation.

The high stability of the crystal is very well explained by the present results, since all the occupied orbitals are strongly bonding. Also for the borides with three-valent metal atoms there is a sufficiently large bonding energy for the extra electron to compensate the ionization energy and the Coulomb repulsion energy, which come in addition. Thus also crystals of this type are very stable. Since in this case there is an odd number of valence electrons in every site, these crystals have large metallic conductivities in good agreement with the experimental facts.

Table 12 shows that the M shell orbitals are very essential for many of the strongly bonding site orbitals. This result confirms the necessity of taking these orbitals into account. When the occupation numbers of the M shell orbitals are large, however, they can be correct only for the order of magnitude, since many of the integrals connecting these orbitals have barely reached their maxima for the largest distance occurring in the expansion over the atomic neighbours (see Fig. 4). The presence of some large occupation numbers for the excited orbitals shows that it is rather doubtful to work with only non-excited atomic orbitals in an attempt to describe the electron distribution in a crystal. Also when introducing some excited orbitals, it is rather dubious if the present method is always acceptable, since it is too laborious to work out and transform all the integrals for a sufficiently large number of neighbours, and also since it is rather impossible to know, if even more excited orbitals should have been taken into account.

Taking into consideration all the rough methods and all the other inevitable approximations used in the present work it is very remarkable that the results really give so extremely good explanations for the properties of the crystal.

APPENDIX

Derivation of an expression for the effective Hamiltonian operator

Let us consider the two-centre integrals occurring in (6):

$$J_{\mathbf{k}} = \sum_{\mathbf{k}'} \langle \mathbf{k}\,\mathbf{k}' \,|\, H^{12} \,|\, \mathbf{k}\,\mathbf{k}' \rangle; \qquad K_{\mathbf{k}} = \sum_{\mathbf{k}'} \langle \mathbf{k}\,\mathbf{k}' \,|\, H^{12} \,|\, \mathbf{k}'\,\mathbf{k} \rangle. \tag{57}$$

For basic site orbitals with equal parities, the factor which corresponds to the normalizing factor of (3) is real. Thus, in introducing the site orbitals according to (3) we can write

$$\psi_{\mathbf{k}'}^{*}\,\psi_{\mathbf{k}'} = \sum_{\mathbf{n}'\mathbf{n}''} \frac{e^{i\,\mathbf{k}'(\mathbf{n}''-\mathbf{n}')}}{V \sum_{\mathbf{m}} e^{i\,\mathbf{k}'\mathbf{m}}\,\Delta_{\mathbf{m}}}\,\phi_{\mathbf{n}'}^{*}\,\phi_{\mathbf{n}''}. \tag{58}$$

This expression occurs in the integrands of both $J_{\mathbf{k}}$ and $K_{\mathbf{k}}$, summed over $\mathbf{k}'$. Thus, let us introduce the notation

$$D_{\mathbf{n}''-\mathbf{n}'} = \lim_{V\to\infty} \frac{1}{V} \sum_{\mathbf{k}'} \frac{e^{i\,\mathbf{k}'(\mathbf{n}''-\mathbf{n}')}}{\sum_{\mathbf{m}} e^{i\,\mathbf{k}'\mathbf{m}}\,\Delta_{\mathbf{m}}} = \tfrac{1}{8} \int_0^{\pi}\!\int_0^{\pi}\!\int_0^{\pi} \frac{e^{i\,\mathbf{k}(\mathbf{n}''-\mathbf{n}')}}{\sum_{\mathbf{m}} e^{i\,\mathbf{k}\mathbf{m}}\,\Delta_{\mathbf{m}}}\, d\,k_1\, d\,k_2\, d\,k_3. \tag{59}$$

Especially for orthogonal site orbitals, it must be realized that

$$D_{\mathbf{n}''-\mathbf{n}'} = \delta_{\mathbf{n}'\mathbf{n}''} \tag{60}$$

is a Kronecker symbol. This is also merely a consequence of the fact that the elements of the one-electron density matrix are invariant for a transformation (3)⇌(4) in the orthogonal case.

By use of the overlap matrix

$$\boldsymbol{\Delta} = \int \boldsymbol{\Phi}^{\dagger}(\mathbf{r})\, \boldsymbol{\Phi}(\mathbf{r})\, d\,\tau, \tag{61}$$

where $\boldsymbol{\Phi}(\mathbf{r})$ is a row matrix with the site orbitals $\phi_{\mathbf{n}}(\mathbf{r})$ as elements, we may construct orthogonal site orbitals $\chi_{\mathbf{n}}(\mathbf{r}) = \chi(\mathbf{r}-\mathbf{n})$ according to the Löwdin [4] formula,

$$\boldsymbol{\chi} = \boldsymbol{\Phi}\,\boldsymbol{\Delta}^{-\frac{1}{2}}, \tag{62}$$

where $\boldsymbol{\chi}$ is a row matrix with $\chi_{\mathbf{n}}$ as elements. On account of (62) we see that

$$\boldsymbol{\psi}\boldsymbol{\psi}^{\dagger}=\boldsymbol{\chi}\boldsymbol{\chi}^{\dagger}=\boldsymbol{\Phi}\boldsymbol{\Delta}^{-1}\boldsymbol{\Phi}^{\dagger} \tag{63}$$

Here $\boldsymbol{\psi}$ is a row matrix of the crystal orbitals, $\psi_{\mathbf{k}}$. Summing over $\mathbf{k}'$ in (58) yields

$$\boldsymbol{\psi}\boldsymbol{\psi}^{\dagger}=\boldsymbol{\Phi}\,\mathbf{D}\,\boldsymbol{\Phi}^{\dagger} \tag{64}$$

where the elements of $\mathbf{D}$ are given by (59). Comparing (63) and (64), which can be considered as the unity operator in Hilbert space, we see that $\mathbf{D}=\boldsymbol{\Delta}^{-1}$. Now, from (64)

$$\sum_{\mathbf{k}'}\psi^{*}_{\mathbf{k}'}(\mathbf{r}')\,\psi_{\mathbf{k}'}(\mathbf{r}'')=\sum_{\mathbf{n}',\mathbf{n}''}D_{\mathbf{n}''-\mathbf{n}'}\,\phi^{*}_{\mathbf{n}'}(\mathbf{r}')\,\phi_{\mathbf{n}''}(\mathbf{r}'')\,. \tag{65}$$

Formally, this is an element of the charge density matrix, although the sum here goes over all $\mathbf{k}'$. Using (65) and (3), (57) gives

$$\left.\begin{aligned}
J_{\mathbf{k}}&=\Big(V\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}\Delta_{\mathbf{m}}\Big)^{-1}\sum_{\substack{\mathbf{m}',\mathbf{m}''\\ \mathbf{n}',\mathbf{n}''}}e^{i\mathbf{k}(\mathbf{m}''-\mathbf{m}')}D_{\mathbf{n}''-\mathbf{n}'}\langle \mathbf{m}'\,\mathbf{n}'\,|H^{12}|\,\mathbf{m}''\,\mathbf{n}''\rangle;\\
K_{\mathbf{k}}&=\Big(V\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}\Delta_{\mathbf{m}}\Big)^{-1}\sum_{\substack{\mathbf{m}',\mathbf{m}''\\ \mathbf{n}',\mathbf{n}''}}e^{i\mathbf{k}(\mathbf{m}''-\mathbf{m}')}D_{\mathbf{n}''-\mathbf{n}'}\langle \mathbf{m}'\,\mathbf{n}'\,|H^{12}|\,\mathbf{n}''\,\mathbf{m}''\rangle.
\end{aligned}\right\} \tag{66}$$

For orthogonal site orbitals, these formulae are in accordance with those given by Wohlfarth [18]. However, since V is the infinite number of sites in the crystal, it is convenient to reduce these expressions furthermore. As a matter of fact, the integrals in the site orbital space do not change their values, if all the centres, which occur in the integrals are changed by a common translation belonging to the total symmetry group of the crystal. Thus, it is allowed to subtract the vector $\mathbf{m}'$ from all the four site indices of every term in (66) without changing the result. Hence, if we make the substitutions $\mathbf{m}''=\mathbf{m}+\mathbf{m}'$, $\mathbf{n}'=\mathbf{p}'+\mathbf{m}'$ and $\mathbf{n}''=\mathbf{p}''+\mathbf{m}'$ into (66) we see that the expressions inside the sums are independent of $\mathbf{m}'$. Thus, the summation over $\mathbf{m}'$ gives a factor V, which is shortened by the factor $1/V$. Hence we can write

$$J_{\mathbf{k}}=\frac{\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}J_{\mathbf{m}}}{\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}\Delta_{\mathbf{m}}};\qquad K_{\mathbf{k}}=\frac{\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}K_{\mathbf{m}}}{\sum_{\mathbf{m}}e^{i\mathbf{k}\mathbf{m}}\Delta_{\mathbf{m}}}, \tag{67}$$

where

$$J_{\mathbf{m}}=\sum_{\mathbf{p}'\mathbf{p}''}D_{\mathbf{p}''-\mathbf{p}'}\langle 0\,\mathbf{p}'\,|H^{12}|\,\mathbf{m}\,\mathbf{p}''\rangle \tag{68}$$

and

$$K_{\mathbf{m}}=\sum_{\mathbf{p}'\mathbf{p}''}D_{\mathbf{p}''-\mathbf{p}'}\langle 0\,\mathbf{p}'\,|H^{12}|\,\mathbf{p}''\,\mathbf{m}\rangle. \tag{69}$$

In the special case of orthogonal site orbitals there is found

$$J_{\mathbf{m}}=\sum_{\mathbf{n}}\langle 0\,\mathbf{n}\,|H^{12}|\,\mathbf{m}\,\mathbf{n}\rangle \tag{70}$$

and

$$K_{\mathbf{m}}=\sum_{\mathbf{n}}\langle 0\,\mathbf{n}\,|H^{12}|\,\mathbf{n}\,\mathbf{m}\rangle. \tag{71}$$

In the general case we can introduce the following notation (cf. (6)):

$$F_{\mathbf{n}} = H^1_{\mathbf{n}} + \lambda_1 J_{\mathbf{n}} - \lambda_2 K_{\mathbf{n}}. \tag{72}$$

This gives the expression (10) of $\varepsilon_{\mathbf{k}}$. By using (11) for the site orbitals, the equation (12) is formally unchanged, if we use the following expression for $F^{\nu'\nu''}_{\mathbf{k}}$:

$$F^{\nu'\nu''}_{\mathbf{k}} = \sum_{\mathbf{n}} e^{i\mathbf{kn}} \left\{ \left\langle \begin{matrix}\nu' \\ \mathbf{m}\end{matrix} \right| H^1 \left| \begin{matrix}\nu'' \\ \mathbf{m}+\mathbf{n}\end{matrix} \right\rangle + \sum_{\mu'\mu''} C^*_{\mu'} C_{\mu''} \sum_{\mathbf{n}'\mathbf{n}''} D_{\mathbf{n}''-\mathbf{n}'} \times \right.$$
$$\left. \times \left[\lambda_1 \left\langle \begin{matrix}\nu' & \mu' \\ \mathbf{m} & \mathbf{n}'\end{matrix} \right| H^{12} \left| \begin{matrix}\nu'' & \mu'' \\ \mathbf{m}+\mathbf{n} & \mathbf{n}''\end{matrix} \right\rangle - \lambda_2 \left\langle \begin{matrix}\nu' & \mu' \\ \mathbf{m} & \mathbf{n}'\end{matrix} \right| H^{12} \left| \begin{matrix}\mu'' & \nu'' \\ \mathbf{n}'' & \mathbf{m}+\mathbf{n}\end{matrix} \right\rangle \right] \right\}. \tag{73}$$

The site indices have been put below the orbital indices in the one- and two-electron integrals above. Since the coefficients C_μ occur in (73), $F^{\nu'\nu''}_{\mathbf{k}}$ are not independent of the variation in (14).

In the Hartree approximation the Fock operator working in the φ space now can be written

$$F = H^1 + \lambda_1 \sum_{\mu'\mu''} C^*_{\mu'} C_{\mu''} \sum_{\mathbf{n}'\mathbf{n}''} D_{\mathbf{n}''-\mathbf{n}'} \int \varphi^{\mu'*}_{\mathbf{n}'}(2) \frac{1}{r_{12}} \varphi^{\mu''}_{\mathbf{n}''}(2)\, d\tau_2. \tag{74}$$

By use of (74) we find the elements, which in the one-electron approximation are replaced by the energy elements $h^{\mu\nu}_{\mathbf{k}}$ of (15):

$$F^{\mu\nu}_{\mathbf{k}} = \sum_{\mathbf{n}} e^{i\mathbf{kn}} \int \varphi^{\mu*}(1)\, F\, \varphi^{\nu}_{\mathbf{n}}(1)\, d\tau_1. \tag{75}$$

The effective one-electron Hamiltonian operator (38) corresponds to the Fock operator given above with suitably chosen coefficients C_μ and the inverse overlap matrix **D** replaced by the unity matrix.

ACKNOWLEDGMENTS

The author is much obliged to the head of this institute, Professor O. Klein, for his stimulating interest and for his kindness in supporting this investigation by permitting the use of the resources of the institute. Furthermore, I want to express my sincere gratitude to Dr. I. Hjalmars, who has proposed this investigation and who has been very helpful and encouraging as the work proceeded. I am very grateful to Professor M. A. Melvin, Dr. G. G. Hall, Dr. Chr. Klixbüll-Jørgensen and Dr. P. O. Löwdin, who have been kind enough to read this paper with critical eyes, and who have made many valuable comments on details. For valuable discussions I am also much obliged to fil. lic. B. Laurent. For assistance with some of the numerical work at desk machines I am very thankful to Mr. L. Norén. For some valuable help in connection with the numerical work at Besk the author is thankful to fil. lic. G. Kjellberg, Dr. G. Dahlquist, fil. kand. B. Alenius, fil. kand. K. G. Bergstrand and many others. For free machine time at Besk the author is grateful to *Statens Naturvetenskapliga Forskningsråd*. For assistance with the typing of the manuscript and drawing of the figures my thanks are due to Mrs. F. Ahnborg and Mrs. G. Weiss. For examining the English I want to thank my cousin, Mrs. M. de Cabrera.

Institute of Theoretical Physics, University of Stockholm, May 1958.

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Tryckt den 17 januari 1959

Uppsala 1959. Almqvist & Wiksells Boktryckeri AB